AN ASSESSMENT OF SOURCES, PATHWAYS, MECHANISMS AND RISKS OF CURRENT AND POTENTIAL FUTURE POLLUTION OF WATER AND SEDIMENTS IN GOLD-MINING AREAS OF THE WONDERFONTEINSPRUIT CATCHMENT

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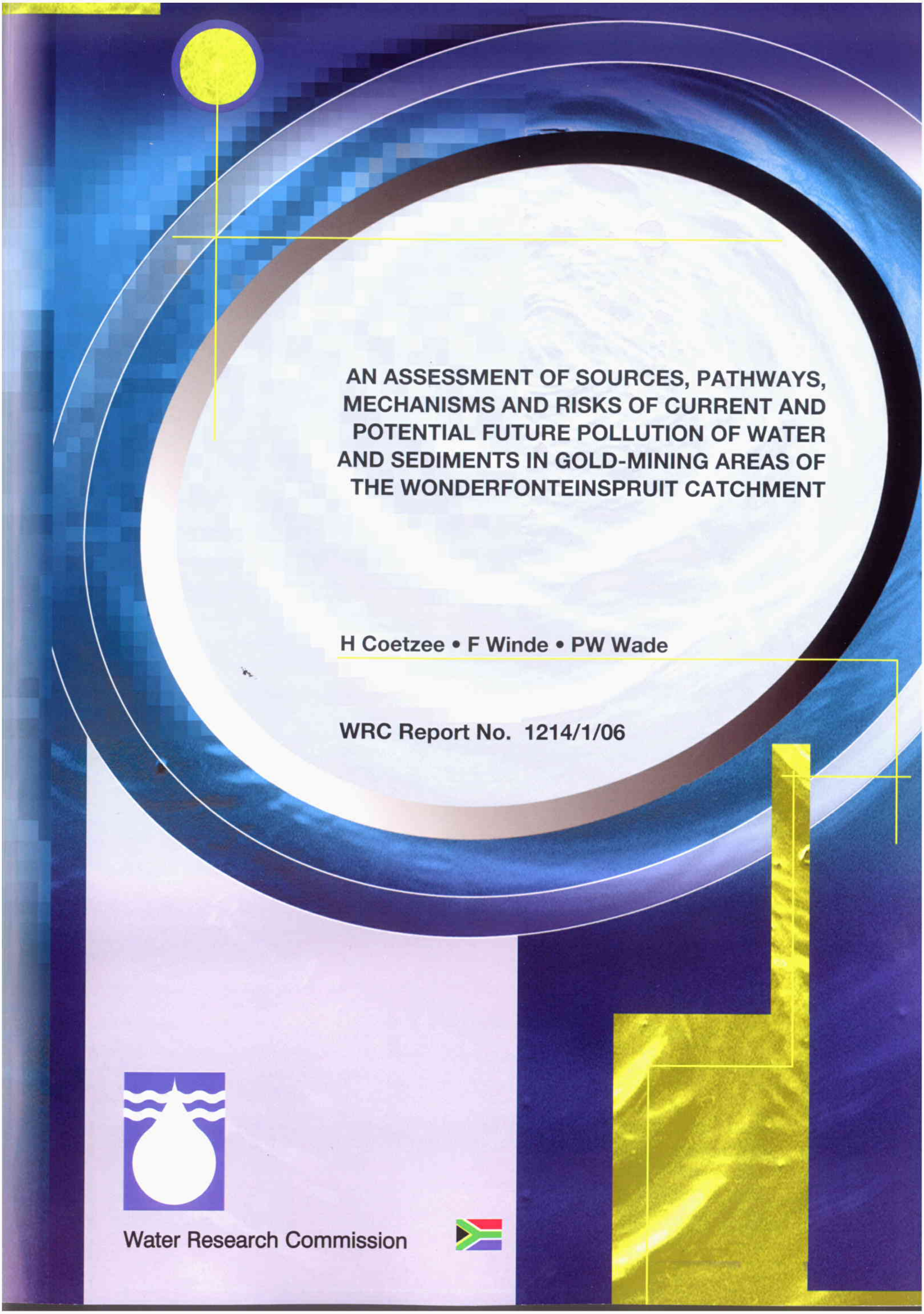
WRC Report No. 1214/1/06

Water Research Commission



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Report to the

WATER RESEARCH COMMISSION

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Reference to the **whole of the publication** should read:
Coetzee, H. (compiler) 2004: An assessment of sources, pathways, mechanisms and risks
of current and potential future pollution of water and sediments in gold-mining areas
of the Wonderfonteinspruit catchment
WRC Report No 1214/1/06, Pretoria, 266 pp.

Reference to chapters/sections within the publication should read (example):
Wade, P., Winde, F., Coetzee, H. (2004): Risk assessment. In: Coetzee, H (compiler): An assessment of
sources, pathways, mechanisms and risks of current and potential future pollution of water
and sediments in gold-mining areas of the Wonderfonteinspruit catchment.
WRC Report No 1214/1/06, pp 119-165

WRC Report No 1214/1/06
ISBN No 1-77005-419-7

MARCH 2006

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.

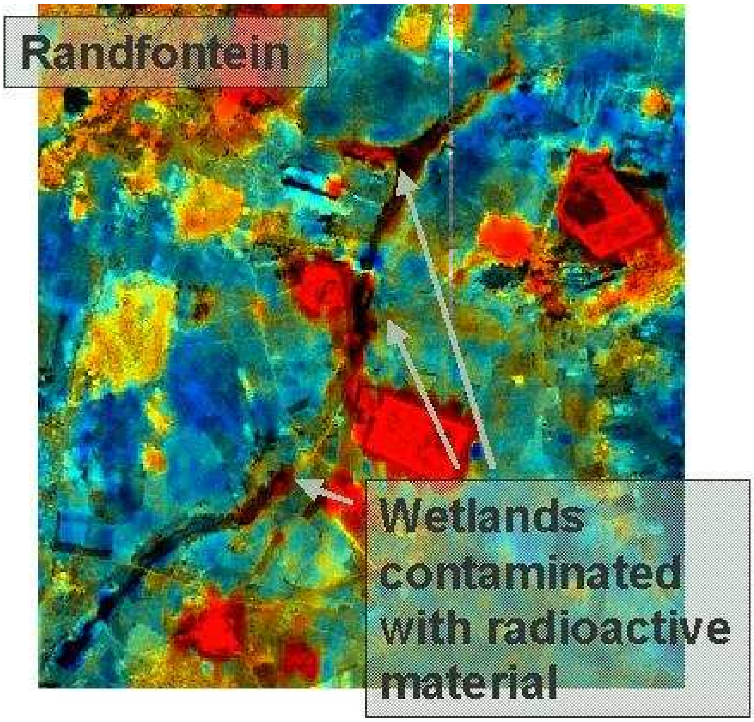
With the establishment of West Rand Consolidated in 1887 gold mining reached the Wonderfonteinspruit catchment only one year after the discovery of gold on the Witwatersrand. By 1895 five more gold mines had started operations in the (non-dolomitic) headwater region of the Wonderfonteinspruit as the 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.

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[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 (δ^{87}Sr) vs. that of sulphur (δ^{34}S), as well as of δ^{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.

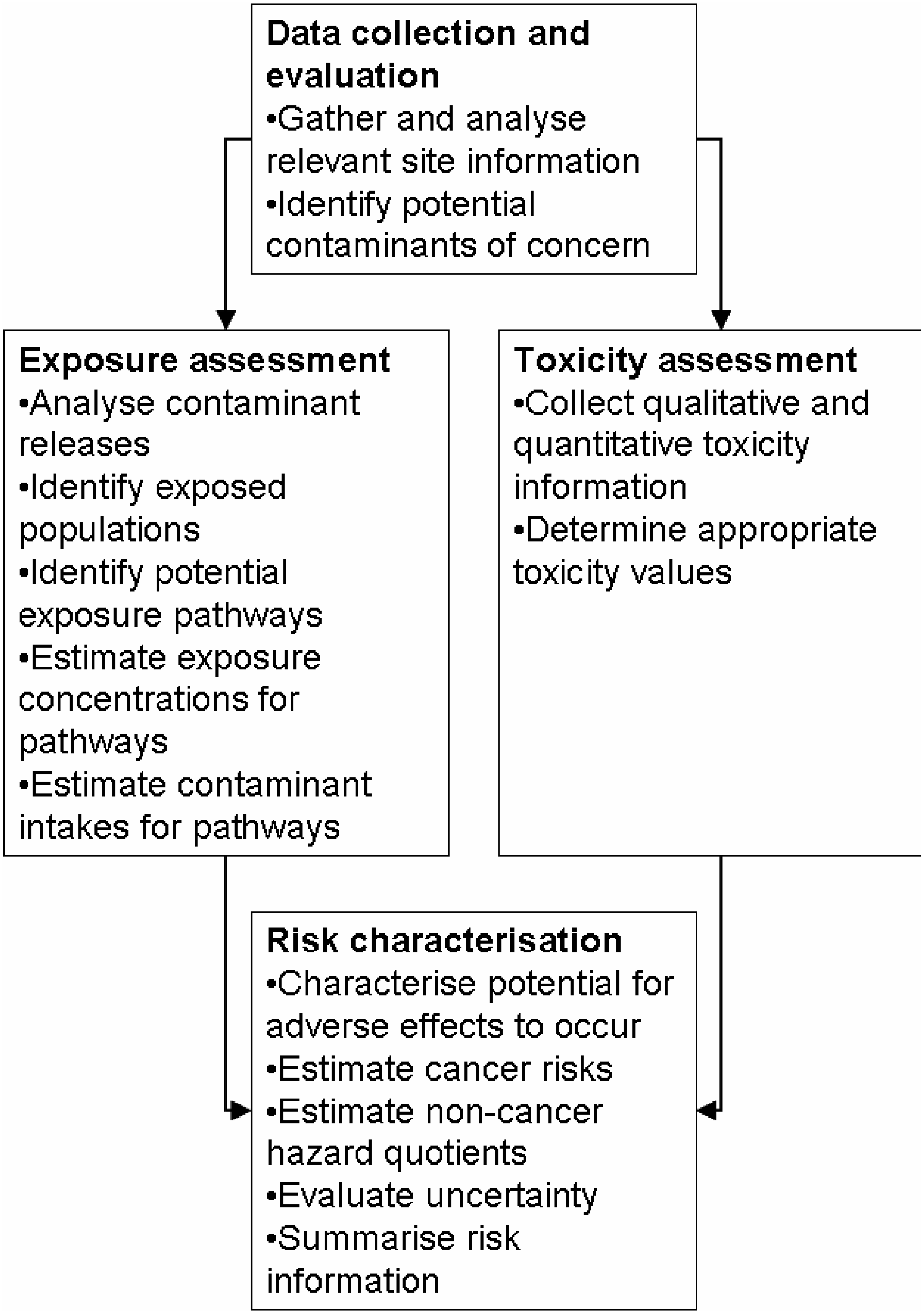
Since current sampling protocols do not consider the temporal variations of uranium concentration in stream water, appropriate adjustments should be made in order to comprehend the actual extent of uranium transport. Future real-time measurements should include electronic probes for measuring rainfall (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.

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    - 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.

ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission entitled :

“The assessment of current and future water pollution risks due to gold mining in dolomitic areas”.

The Steering Committee responsible for the project consisted of the following persons :

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Mr H M du Plessis	Water Research Commission
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Mr J F Ellis	AngloGold Ashanti
Dr K Jutle	NNR
Mr M Keet	DWAF

The financing of the project by the Water Research Commission and the contribution of the members of the Steering Committee are acknowledged gratefully.

DISCLAIMER BY THE NATIONAL NUCLEAR REGULATOR

The National Nuclear Regulator (NNR) is an independent statutory body mandated to protect persons, property and the environment from nuclear damage through the establishment of safety standards and regulatory practices.

The NNR has considered the report of the Water Research Commission relating to the water pollution risk of the Mooirivierloop, and comments thereon as follows:

The NNR makes use of an internationally recognized methodology as well as international norms and standards in its radiological risk assessment of uranium levels in water. The methodology used by the WRC in this report is inconsistent with these norms and standards. Its research essentially assesses the chemical risk of uranium in the water body.

In the circumstances, the NNR is not in a position to concur with the methodology and conclusion of this report.

The NNR is undertaking its own investigation and will make the findings available to the public.

Enquiries in this regard can be addressed to the National Nuclear Regulator, Mr C O Phillips, at P O Box 7106, Centurion, 0046
Tel: 012 674 7100, Fax: 012 6635513.

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1 Introduction

1.1 The Wonderfonteinspruit catchment (H. Coetzee)

The Wonderfonteinspruit catchment, as it has come to be known, comprises the eastern catchment of the Mooi River. The main drainage channel is known at various points as the Mooirivierloop and Wonderfonteinspruit. For the purposes of this report, the catchment, as indicated on Figure 1, will be referred to as the Wonderfonteinspruit.

The Wonderfonteinspruit has its source at the Continental Divide in the Krugersdorp area. From here it flows past Kagiso, Azaadville and Randfontein into Donaldson Dam near Westonaria. At Donaldson Dam, the flow of the river is channeled into a large pipeline, which carries the water over the dolomitic groundwater compartments until it discharges near Carletonville. This diversion of the river from its natural channel has been done to allow deep gold mining to proceed below the outcropping dolomite.

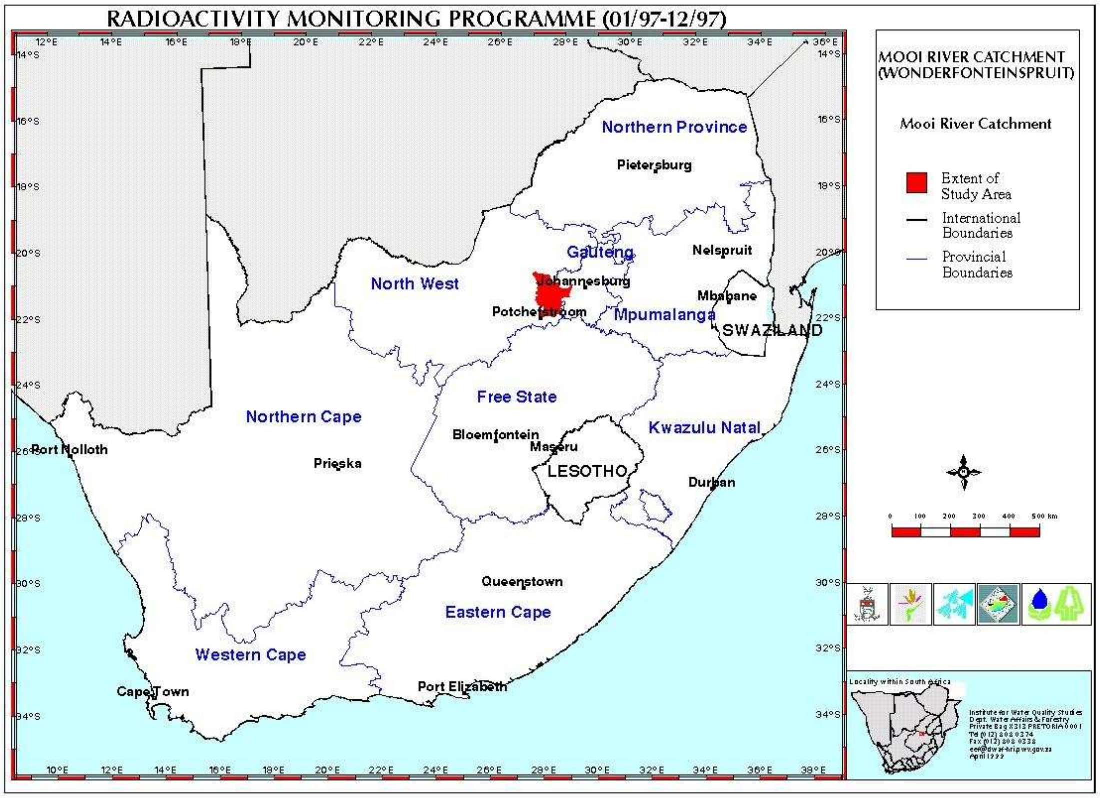

Figure 1. Locality of the Mooi River catchment, including the Wonderfonteinspruit (IWQS, 1999)

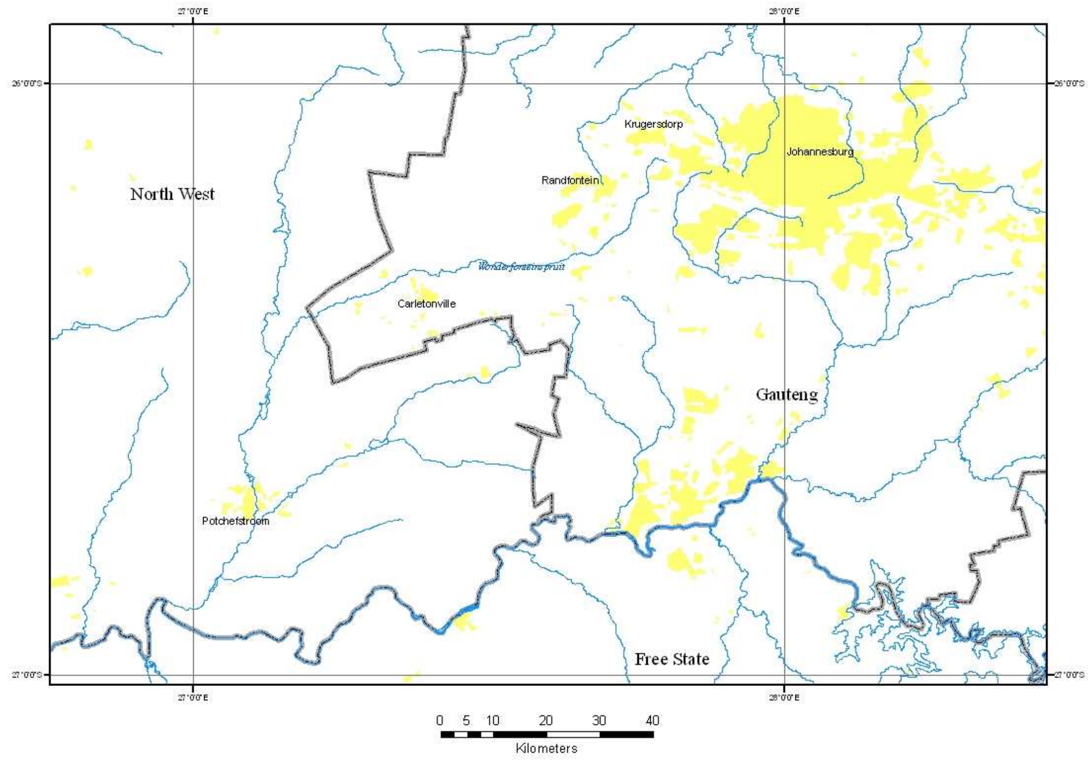

Figure 2. Locality plan of the Wonderfonteinspruit and surrounding area.

1.2 Gold and uranium mining in the Wonderfonteinspruit catchment and environs (F. Winde)

1.2.1 Goldfields and gold mines of the area

The catchment of the Wonderfonteinspruit covers parts of two goldfields of the Witwatersrand basin, namely the western part of the ***'West Rand' goldfield*** in its upper region of the catchment with mines such as East Champ d'Or, Luipaardsvlei Estates, First Wits Gold Mine and Randfontein Estates (Randfontein, Doornkop, Cook and Millsite section), and the '***Far West Rand' goldfield*** at the left-hand side of lower Wonderfonteinspruit (downstream of Donaldson Dam). The latter consists of an area called ***'West Wits Line',*** comprising gold mines near the town of Westonaria (Venterspost, Libanon, Kloof, Western Area, South Deep) and the '***Carletonville mining area'*** with mines such as Blyvooruitzicht, Doornfontein, West and East Driefontein, Elandsrand, Deelkraal and Western Deep Levels (Robb and Robb, 1998).

After exploration activities in the area between 1899 and 1904, first attempts to mine discovered gold reefs were hampered by inrushes of groundwater into sunken shafts. It was only during the 1930s that an appropriate cementation technology for coping with excess water allowed for deep-level gold mining in this region to commence. Aided by a newly developed magnetic prospecting technology, eventually 10 gold mines were established. Averaging 31 mg/kg gold grade over its history, the Far West Rand proved to be the richest of all seven actively mined goldfields in the Witwatersrand basin (Cole, 1998). Some of the richest gold mines of the world are located here, producing about eight times more gold than the West Rand in the upper part of the Wonderfonteinspruit catchment (Wymer, 1999).

1.2.2 Gold deposition

Gold is mainly extracted from relatively narrow bands of quartzitic conglomerates (so-called 'reefs'), which were deposited as fluvial sediments in river deltas at the shores of an ancient inland lake of some 250 km in diameter almost three billion years ago. The sediments eventually filled the lake, which later became known as 'Witwatersrand basin'. Since there was a heavy impact by tectonic and volcanic activity during the course of time, as well as by further deposition of sediments, the lake sediments eventually tilted towards the southeast, exposing the northwesterly edge of the sediment layers to the surface. Having been metamorphosed into solid rock strata, these sediment layers formed prominent weathering-resistant outcrops at which gold mining originally started. Today's gold mines follow the auriferous strata dipping towards the centre of the ancient lake, reaching ever-greater depth. With mining nearly 4 km below the surface, Western Deep Levels GM (now called 'West Wits Operations' of Anglogold Ltd) is the world's deepest gold mine, having envisaged projects of ultradeep mining to a depth of more than 6 km to the south of its current lease area.

Mined gold reefs
Relating mainly to tectonically induced differences of their stratigraphic order, sediments deposited in the Witwatersrand basin ('Witwatersrand Supergroup') in this area are divided into two major groups, namely the 'West Rand Group' (named after sediment stratigraphy first encountered in the West Rand) and the overlying 'Central Rand Group', both covered by Ventersdorp lavas ('Ventersdorp Supergroup'). Both groups are subdivided into 'subgroups' and named after the location of their first discovery (e.g. 'Johannesburg Subgroup'). Reefs mined in the West Rand and Far West Rand goldfield are part of the Central Rand Group, e.g. the ***Carbon Leader Reef*** and ***Middelvlei Reef*** (both Johannesburg Subgroup, >3 000 m below surface), and the ***Elsburg Reef*** and ***Composite Reef*** ('Turffontein Subgroup'). In addition, an up to 8-m-thick contact zone between the upper parts of the Witwatersrand sediments and the Ventersdorp lava, known as ***Ventersdorp Contact Reef*** (VCR, 2 000 m below surface), as well as a bituminous conglomerate in even younger strata in the overlying 'Transvaal Supergroup' (***Black Reef,*** 10–<1 000 m below surface) are mined. The latter is the only reef in the area that is developed by open-cast mining (by *First West Rand Consolidated* in the uppermost part of the Wonderfonteinspruit catchment). The groups are separated by far-reaching faults along which the sediments were vertically and/or laterally shifted. A major fault in the Far West Rand area is the N–S-running '*Bank fault'* separating sediments of different alluvial fans, entry points and sources areas, which are now mined by three mines to the east and seven mines to the west of the fault.

The gold in those reefs is believed to originate mainly from eroded auriferous granite domes in the northwesterly hinterland of the rivers and was either transported in particle form (detrital minerals), hydraulically settling where stream velocity decreased (placer deposits in deltas), or in dissolved form precipitating in reducing environments as e.g. found in shallow parts of the lake shores inhabited by colonies of cyano bacteria. With gold and uranium belonging to the heaviest elements naturally occurring on earth and displaying an extremely high density, both elements are often found to be associated in placer deposits (Robb and Robb, 1998).

Influenced not only by gravitational sorting but also by redox-initiated precipitation, the richest reef of the area, the ***Carbon Leader Reef,*** was formed, reflecting tidal, marine conditions. It is named after its high concentrations of carboniferous (bituminous) matter that is believed to originate from decomposed algal mats on sediments. Rarely exceeding 10 cm in thickness, the lowermost 1–2 cm of the reef almost exclusively consist of black bituminous matter of anthracitic, coal-like appearance called ‘kerogen’. Kerogen, also occurring as isolated nodules throughout the overlying quartzitic conglomerates of the reef (‘flying speck’), contains extraordinarily high concentrations of gold (up to 9 100 mg/kg) and uranium. The CLR was particularly well mineralised along the common border between *Blyvooruitzicht GM* and *West Driefontein GM*, and displayed decreasing gold content in the more distal regions of the reef. Only occurring west of the Bank anticline as the deepest of the three mined major gold reefs (>3 200 m below surface), the CLR is now largely mined out (Cole, 1998).

Dolomite

A peculiarity of the Far West Rand area is the presence of carbonate rock (dolomite) covering auriferous Witwatersrand sediments. The up to 1 500-m-thick dolomitic layer formed in a marine environment by calcite precipitation. Exposed to atmospheric weathering the upper 100–200 m of the dolomite is heavily weathered by chemical dissolution, resulting in extensive karstification including the formation of large subsurface cave systems interlinked by solution slots and joints. Being filled with infiltrating rainwater, this upper part of the dolomite acts as a major aquifer. It was water from that aquifer which entered sunken shafts of early mining attempts at the beginning of the 20th century. After being formed the more than 80-km-long and 10–15-km-wide dolomitic layer was divided into several units (‘compartments’) by impermeable syenite/ dolerite dykes that intruded from below during volcanic activities (Swart et al., 2003). To ensure safe underground mining and to minimise pumping costs, some of these compartments were later dewatered by continuously pumping infiltrating groundwater from underlying mine workings to the surface and discharging it outside the dewatered compartments (Swart et al., 2003).

1.3 Uranium mining (F. Winde)

1.3.1 Historical development

Initiated by the ‘Manhattan Project’ of the USA to develop the nuclear bomb in the 1940s, uranium exploration in South Africa started in 1944 when an American expert group screened several thousands of samples of Witwatersrand sediments for the much-needed uranium. Owing to concerted efforts by the South African government and Chamber of Mines of SA, and supported by the USA and Great Britain, large-scale industrial production of uranium commenced soon after that. By 1959 SA already produced 4 950 t uranium entirely used for the atomic-weapon programme. With more than 150 000 t uranium concentrate produced during the

Cold War between 1945 and 1990, SA became the fourth largest uranium producer in the world after Canada, the USA and East Germany (the latter producing uranium for the nuclear-weapons programme of the USSR) (**Cole, 1998; Venter, 2001**). An the peak of uranium production in 1980 SA was the seventh largest uranium producer, with an output of some 7 000 t uranium (Harding in Venter, 2001) (Cole, 1998: 6 146 t).

Compared with primary ore deposits with uranium grades of 0,03–7 per cent (300–70 000 mg/kg) as mined in Canada and Australia, secondary ore deposits associated with phosphates, copper and gold are regarded as low-grade ore with grades ranging from 30–200 mg/kg uranium (**McLean, 1994; Cole, 1998**). Therefore, in SA uranium was mainly (although not exclusively) produced as a by-product of gold, which subsidised mining costs. In 1994 some 96 per cent of the total uranium production of 1 708 t came from gold mines of the Witwatersrand basin, while the remaining 4 per cent was produced as by-product by the copper mine in Phalaborwa (Cole, 1998).

1.3.2 Uranium occurrence

Uranium in gold reefs of SA occurs mainly in brown-blackish tetravalent minerals such as uraninite (UO_2) or pitchblende (an amorphous mixture of UO_2 and U_3O_8), and in oxidised derivates thereof (secondary minerals) such as coffinite ($USiO_4$), brannerite (UTi_2O_6) and leucoxene, the latter being a weathering product of brannerite (Cole, 1998). The extremely heavy uraninite (density: 10,95 g/cm^3) occurs in reefs in the form of small, muffin-shaped weathered particles from uraniferous rocks with a typical diameter of 77–100 µm. Uraninite becomes unstable in the presence of oxygen and tends to release uranium into dissolving agents such as fissure water. Other forms of uranium include a wide range of hexavalent minerals with typically bright yellow, green and orange colours frequently fluorescing under UV-light. Such minerals include carnotite, uranophane, beta-uranophane, tyuyamunite, autunite and torberite. Urano-organic compounds, as a third form of uranium in ores, are frequently present in sedimentary deposits such as black shale and lignite.

The highest uranium concentrations in the area are associated with carbon and were found in kerogen seams and nodules of the ***CLR***, displaying up to ***58 000 mg/kg*** uranium (5,8%). Other uraniferous reefs include the ***Doornfontein Reef*** (which was never exploited because of low gold grades), ***Ventersdorp Contact Reef, Elsburg Reef, Composite Reef*** and quartz-pebble conglomerates of the ***White Reef, Monarch Reef*** and ***Middelvlei Reef*** (<7 m thick, well sorted) (Table 1)**.**

Table 1. Uraniferous reefs and their uranium grades in the Far West Rand (FWR) and West Rand (WR) goldfields (data compiled from Cole, 1998)

Goldfield	**Reef**	***av.* uranium grade** [mg/kg]	**Notes**
FWR	Carbon Leader	145	Max uranium concentration: 58 000 mg/kg
FWR	Doornfontein	340	Not mined owing to low gold grade
FWR	Middelvlei	51	Mined, but uranium not leached
FWR/WR	VCR (upper unit)	126	

Goldfield	**Reef**	***av.* uranium grade** [mg/kg]	**Notes**
FWR/WR	VCR (lower unit)	158	
FWR/WR	Elsburg	383	
WR	Composite	120	
WR	White		Not mined owing to low gold grade
WR	Monarch		Not mined owing to low gold grade

Owing to the comparatively high uranium concentrations in the gold reefs mined earlier on, uranium production in SA was concentrated on the West Rand and Far West Rand goldfields. Uranium in the Far West Rand was exclusively produced from the Carbon Leader Reef, yielding a total of **11 295 t U_3O_8** between 1952 and 1988 at an average uranium grade of 145 mg/kg (Cole, 1998).

The first pilot uranium plant of SA was constructed at Blyvooruitzicht (1951), followed by the first uranium producing uranium plant at West Rand Consolidated (1952) and others across the area including uranium plants at Randfontein Estates, Luipaardsvlei (all in the vicinity of Randfontein), Western Areas (near Westonaria), West Driefontein and Western Deep Levels (located around Carletonville). At one stage **9** out of the 22 active **gold mines** of the region were feeding uraniferous ore into a total of seven **uranium plants (McLean, 1994; Cole, 1998)**.

1.4 Radiometric evidence for sediment contamination (H. Coetzee)

During 1991 the Council for Geoscience undertook high-resolution airborne radiometric surveys of large parts of the Witwatersrand. The primary aim of these surveys was the mapping of the geology, together with the simultaneous collection of magnetic data. It was well known from previous regional-scale surveys that the mine-waste dumps in the Witwatersrand would show significant radiometric anomalies, owing to their elevated concentrations of uranium daughter nuclides. The airborne radiometric method cannot directly detect uranium, but focuses on gamma-emitting radionuclides. In the uranium series, ^{214}Bi is the dominant gamma emitter.

The high-resolution data, showed a new and disturbing trend. Not only did the mine-waste deposits emit significantly more gamma radiation than the surrounding environment, the wetlands downstream of the mining areas were also contaminated. In deposits such as these, the normal assumptions made in airborne radiometric surveying, *i.e.* that the daughters are in secular equilibrium with the parent nuclide and that the deposit has a lateral extent greater than the field of view of the spectrometer detector (typically up to a few hundred metres), are obviously not valid. The anomalies do, however, indicate significant levels of contamination with radioactive material (Coetzee, 1995). In addition to the radionuclides, other metallic contaminants have been located in the radioactively anomalous areas (Coetzee and Szczesniak, 1993). Figure 3 shows a portion of this dataset in a mining area near Krugersdorp.

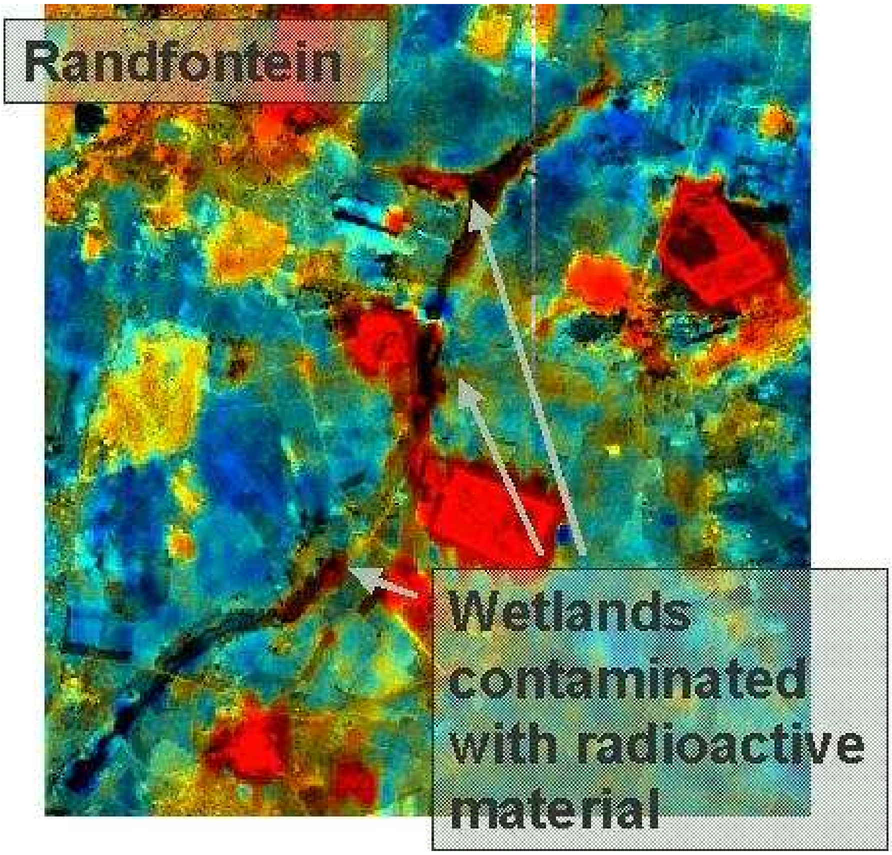

Figure 3. Total-count radiometric image of a portion of the Wonderfonteinspruit catchment, over a Landsat Image background. Red areas indicate elevated radioactivity levels. Note the elevated radioactivity in the wetlands downstream of mining areas

The areas identified in this study correlate well with the sites found to have high radionuclide levels by Wade et al. (2002).

1.5 Background to this project (H. Coetzee and P. Wade)

During 1997, an intensive sampling programme was undertaken in the Wonderfonteinspruit catchment (See Figure 2). In this study, it was found that mining activities in the area are a major contributor to the radionuclide content of the water, specifically with respect to uranium and uranium-series nuclides, but that the activities of dissolved radionuclides decrease downstream of mining activities. Following this finding, Wade et al. (2002) undertook a study funded by the Water Research Commission to investigate the fate and transport of selected radionuclides within the catchment.

This second study indicated that radionuclides were concentrated in the wetland sediments throughout the catchment, but that the processes concentrating the radionuclides were reversible. Using a combination of chemical modelling and experimental studies, Wade et al. (2002) demonstrated that changes in the geochemical environment within the catchment could remobilise radionuclides, potentially leading to contamination of downstream water resources.

This potential for downstream contamination was identified as a specific concern for the water supply of the City of Potchefstroom. The Potchefstroom City Council therefore requested a detailed follow-up to these studies, looking at uranium and heavy metals in the dam on the farm Blaauwbank. This dam was selected as it is the first dam downstream of all mining activities in the catchment, and was judged to be critical to the protection of the water supply for Potchefstroom. The Council for Geoscience was commissioned to undertake this study, which had three major conclusions:

1. The study confirmed the results for uranium of Wade et al. (2002), with uranium concentrations of several hundred mg/kg being found in the sediment (the expected natural background concentration for a dolomitic area such as this would be less than 1 mg/kg).

2. The study also identified a number of other heavy metals of concern, and noted that these appeared to follow the same behaviour as the radionuclides described by Wade et al. (2002).

3. Based on laboratory studies and chemical modelling, the metals (uranium-series radionuclides are all metals, and behave chemically as such in the environment) are adsorbed or chemisorbed to a number of sediment phases, all of which can be re-released by plausible geochemical processes.

These two studies on sediment concluded that while current conditions were relatively stable, albeit not totally effective in removing metals from the water, the unpredictability of the future required management plans that would either maintain conditions as they were *ad infinitum* or would have to contemplate rehabilitation of the contaminated areas within the environment.

Following the production of the second report on sediments, the dam in question was drained, exposing the sediments to an oxidising environment (See Figure 4), one of the rerelease scenarios described in the report. At this point, the Potchefstroom City Council took legal action against one of the gold mines responsible for the contamination. This case was settled out of court, with the mine agreeing to rebuild the dam wall and to rehabilitate the environment.

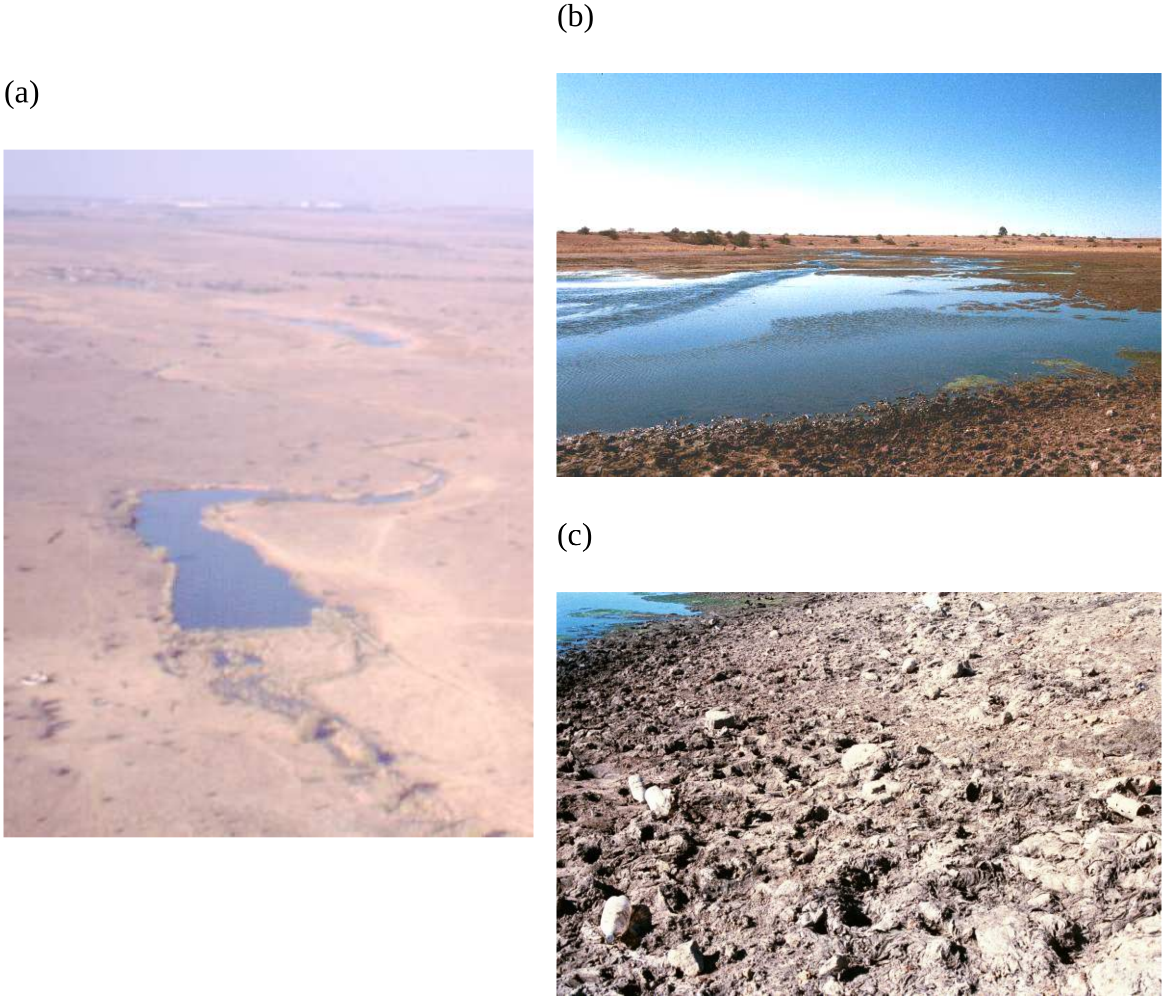

Figure 4. Andries Coetzee’s Dam: (a) prior to draining in January 2003 (Photo Winde, 2001), (b) after draining and (c) close-up of the dried-out sediment exposed to oxidation (photos: H Coetzee).

1.6 *Scope of this report (H. Coetzee)*

The scope of this study is described in the initially proposed aims, as submitted to the Water Research Commission:

> “The proposed research aims to answer a number of the unanswered questions surrounding the Wonderfonteinspruit. Available monitoring data indicate contamination by mining activities, but, with the exception of a one-year DWAF study on radioactivity, this has not yet been expressed in terms of risk. Furthermore, the findings of Dr Wade's WRC-funded study in 1999 have not been incorporated into the findings regarding radiation doses.

> The Wonderfonteinspruit system has pollution inputs from a large number of sources. The specific contributions of these sources to current pollution in the water and to historical pollution recorded in the sediments will be determined, using isotopic studies on water and sediments.
>
> The project will :
>
> produce an inventory of contaminated sediments to include locations, volumes and the total reservoir of radionuclides, as well as other toxic components;
>
> look at the potential for the liberation of these toxins from the sediments, given the potential variations in physicochemical conditions in the river; and
>
> establish a real-time monitoring capacity for the short-term variations in physicochemical parameters and monitor these continuously for a significant time period.
>
> Determine the contributions of the different source areas and, where possible, individual sources to the polluted waters and sediments within the catchment.
>
> These data will provide input to future remediation plans for the catchment."

This project addresses these aims in the following areas:

1.6.1 Produce an inventory of contaminated sediments, to include locations, volumes and the total reservoir of radionuclides, as well as other toxic components

The inventory of contaminated sediments has been addressed by the review work, found in Sections 2 (Impacts of gold-mining activities on water availability and quality in the Wonderfonteinspruit catchment (F. Winde)) and 3 (Inventory of uranium sources and pathways in the catchment (F. Winde)), as well as the sampling and analysis of samples from the catchment, described in Section 4 (Identification of contaminants and contaminated sites (H. Coetzee and G. Ntsume)). The determination of sediment volumes as originally proposed was found to be impracticable, owing to the difficulty of geophysical surveying of many of the wetland areas, as well as the inaccessibility of many of the wetland areas to drilling equipment. The total reservoir of uranium was, however, indirectly determined by estimating fluxes into the catchment in Section 3 (Inventory of uranium sources and pathways in the catchment (F. Winde)). Since uranium was found to be the contaminant of most concern in the risk-assessment section of this document, it will provide a conservative identification of risk areas for other toxic components of the waste streams entering the Wonderfonteinspruit. Uranium is identified in the project as the contaminant of concern in Section 4.3 (Identification of contaminants of concern) by comparing concentrations in both water and sediment with health-based guidelines for a number of metals.

1.6.2 *Look at the potential for the liberation of these toxins from the sediments, given the potential variations in physicochemical conditions in the river*

The potential for the liberation of metals from the sediments in the Wonderfonteinspruit has been addressed using theoretical as well as laboratory methods. The theoretical aspects of uranium transport are discussed in Sections 3.3 (Pathways and mechanisms of uranium migration from mining sources into the environment), 3.4 (Transport of uranium along the aqueous pathway), 3.5 (Transport of dissolved uranium within the fluvial system) and 9.5 (Environmental chemistry of uranium), and the laboratory investigation in Section 7 (Speciation determination of heavy metals and uranium ─ BCR Protocol Sequential Extraction (H. Coetzee, M. Rademeyer and G. Ntsume)).

1.6.3 *Establish a real-time monitoring capacity for the short-term variations in physico-chemical parameters and monitor these continuously for a significant time period.*

A high-frequency (3–10 min) monitoring station was established at a monitoring station in the Wonderfonteinspruit catchment. The station provided near-continuous data for about half a year. These data are used to determine physicochemical variations in the river water. The origins and possible effects of these variations are described and interpreted. This is described in Section 8 (Temporal variation in hydrochemistry of stream water ─ results of a continuous monitoring study (F. Winde, H. Coetzee and G. Ntsume)).

1.6.4 *Determine the contributions of the different source areas and, where possible, individual sources to the polluted waters and sediments within the catchment.*

Isotopic studies were undertaken to identify possible source areas for the pollution using lead-isotopic analysis of selected sediment samples (See Section 5 Source apportionment ─ Radiogenic lead-isotopic study of selected sediment samples from the catchment (H. Coetzee and M. Rademeyer)), as well as sulphur and strontium isotopes in the dissolved fraction in water (See Section 6 Identification of sources of Wonderfonteinspruit river water using sulphur and strontium isotopes (U. Horstmann and M. Rademeyer)). Owing to the complexity of the system and limited resources for expensive isotopic analyses, it was not possible to resolve the sources to the level of individual mines; however, it is possible to discriminate between different areas within the catchment.

1.6.5 *Future remediation plans*

A definite aim of the project is to feed information into the future remediation of the environmental impacts of more than a century of mining. For this reason, the conclusions and recommendations (Section 10 Conclusion and recommendations (H. Coetzee)) are expressed in terms which could assist in these actions.

1.6.6 Additional areas covered by the project:

As part of the identification of the theoretical aspects controlling remobilisation of metals from sediments, it was possible to identify the mechanisms which could result in the observed elevated uranium and other heavy-metal concentrations in fluvial sediments in the Wonderfonteinspruit catchment.

The final compilation of the data collected by reviewing the available literature, as well as sampling and analysis, has been expressed in terms of a risk assessment. This risk assessment evaluates data to identify potential risks to the environment and downstream water users, using the United States Environmental Protection Agency's Risk Assessment Guidelines for Superfund (RAGS). The full risk assessment is presented in Section 9 (Risk assessment (P. Wade, F. Winde and H Coetzee)).

During the course of the project the title was amended, changing the scope of the project to emphasise methodological development. At the final steering-committee meeting, it was felt that the results were better represented as a risk assessment than a methodological study. It is nevertheless hoped that the methodology presented in this report is suitably rigorous and generic to be applied in other catchments. An outline of this methodology is presented in Section 10.6 (Methodological considerations).

2 Impacts of gold-mining activities on water availability and quality in the Wonderfonteinspruit catchment (F. Winde)

This chapter focuses on uranium as a contaminant, using values published in the literature. In Section 4.3 (Identification of contaminants of concern), uranium is identified as the principal contaminant of concern, using a tier 1 risk approach, as described by Wade *et al.* (2002). Other contaminants have been detected in the same waste streams. The interpretation of these data have been performed by the author, based on first prinpciples.

Many gold mines in the area are located on top of a quartzitic ridge called the 'Gatsrand' that runs in northeast–southwest direction. Elevated by some 100–300 m above adjacent valleys, this ridge forms the watershed between the Wonderfonteinspruit (to the north) and the Loopspruit (to the south). While some lease areas of gold mines of the Far West Rand fall almost completely into the drainage basin of the Wonderfonteinspruit, e.g. those of Venterspost GM (now part of Kloof GM), Blyvooruitzicht and Doornfontein GM (now merged into 'Blyvooruitzicht GM), others stretch across the watersheds into neighbouring catchments, e.g. those of Driefontein Cons. (consisting of formerly separated West and East Driefontein GMs), Kloof GM (in its original extent before merging), Savuka GM and Tautona GM (both part of West Wits Mines, formerly known as Western Deep Levels). A few mines of the Far West Rand fall outside the drainage area of the Wonderfonteinspruit and drain into adjacent catchments of the Klip River and Rietspruit (Western Areas), as well as the Loopspruit (Elandsrand, Deelkraal) (now merged into the Elandskraal GM) and Mponeng GM (the southernmost one of the West Wits Mines) (GSG, 2002).

Having established this, it needs to be pointed out that surface catchment borders do not necessarily coincide with subsurface drainage areas. Therefore inflow of groundwater from adjacent (surface) catchments into the Wonderfonteinspruit system, as well as outflow of groundwater into neighbouring (surface) drainage basins, needs to be considered when determining water balance. This may also be of importance when assessing the potential pollution, e.g. by seepage from tailings dams. Despite being deposited outside the surface catchment, seepage from some slimes ─ especially those located rather close to the watershed ─ may reach the Wonderfonteinspruit via underground mine workings and pumping schemes, and/or other routes of subsurface flow.

2.1 Impacts associated with the dewatering of dolomitic groundwater compartments

Owing to increased volumes of dolomitic groundwater infiltrating into underlying mine workings where fissures and faults were progressively intersected, and because of the associated costs for pumping this so-called *'fissure water'* back to the surface, as well as for safety reasons, gold mines of the Far West Rand in the late 1950s officially proposed the dewatering of overlying dolomitic aquifers to governmental authorities. After a subsequently launched investigation, jointly conducted by a total of 10 governmental authorities (*inter alia* involving the departments of Mining, Water, Agriculture) (pers. commun. Stoch, E.J., 2003), the implementation of dewatering was recommended ─ mainly based on macro-economical considerations (Jordaan et al., 1960). Based on this and a subsequent agreement between the government and involved mines to collectively deal with arising consequences[3], large-scale dewatering officially started in the area in the mid-1960s. However, the Venterspost compartment had been partly dewatered by operating gold mines several years prior to this decision (pers. commun. Stoch, E.J., 2003). By continuously pumping more groundwater from underground mine workings than was naturally recharged by infiltrating rainwater, and discharging the pumped water outside the (surface) boundaries of drained compartments, the groundwater table was gradually lowered until the affected dolomitic aquifers effectively were empty. Starting with the Venterspost compartment, dewatering was then extended to the Oberholzer compartment, followed by the Bank compartment, and concluded with the Gemsbokfontein compartment in the 1980s (pers. commun. Stoch, E.J., 2003). Except for the latter, which is located in the upper Wonderfonteinspruit, all dewatered compartments are located in the lower Wonderfonteinspruit (Venterspost, Bank and Oberholzer Compartment). Ongoing pumping maintains the dewatered status to this date.

The dewatering of dolomitic compartments not only affects groundwater, but also the availability and quality of surface-water resources. Consequences include:

- The lowering of the groundwater table caused dolomitic springs that used to feed into the Wonderfonteinspruit to dry up. This, in turn, significantly reduced stream- flow volumes and increased flow variability downstream of affected springs. The flow regime of that part of the lower Wonderfonteinspruit where it successively traverses the three dewatered compartments is most severely affected. Later this entire reach of the stream was diverted into a pipeline.

- The accelerated formation of sinkholes as one consequence associated with dewatering provided additional conduits for infiltrating rainwater and increased groundwater recharge rates. This, in turn, lowered the surface run-off component and additionally reduced the stream flow.

- The lowering of the groundwater table also caused boreholes of farmers to fall dry. Associated water shortages subsequently led to changes of agricultural land-use patterns. This, in turn, is likely to have altered run-off coefficients and base-flow volumes of affected areas. For example, changing from irrigation crops with high return-flow volumes in the form of seepage to rain-fed crops with low return flow may have resulted in a reduced base-flow contribution to stream flow.

- The construction of new (open) concrete canals, to divert abstracted fissure water from mine shafts to farmers in order to compensate for lost borehole water, is likely to result in increased water losses through evaporation and leakages from broken canals.

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[3] For this purpose the Far West Rand Dolomitic Water Association –FWRDWA- was founded.

- Reduced stream flow in reaches of the Wonderfonteinspruit is likely to have had an adverse impact on natural riparian wetland areas dependent on surface water[4]. Consequences of reducing wetland areas include*:*

    - Increased stream-flow variation due to lower base-flow contributions from wetland areas in dry periods and lower capacity to retain floods;

    - Loss of habitats for a wide range of aquatic organisms, disturbing the functioning of aquatic ecosystems (food chains);

    - Reduced capacity for natural self-purification of the stream, e.g. by settling of suspended solids, adsorption of dissolved metals onto highly sorptive wetland sediments, etc.

- The lowering of groundwater tables in compartments modified subsurface hydraulic gradients, and may result in increased inflows of groundwater from adjacent compartments via fractures and faults in separating dykes.

2.2 *Impacts associated with point discharges of mine effluents*

2.2.1 *Discharge of fissure water from underground mine workings*

Most of the fissure water that is pumped to the surface is discharged via canal systems into the Wonderfonteinspruit. Consequences of the pointdischarge of large volumes of fissure water into the stream include:

Creation of artificial flow regimes below the point of discharge
Because of price differences between peak and off-peak electricity, pumping rates display distinct day–night differences resulting in pronounced diurnal variations of discharge volumes and associated stream flow below the point of discharge. In contrast, the seasonal fluctuation of stream flow, often important for natural ecosystems to thrive, is markedly reduced by continuously discharging water throughout the year at a more or less constant rate. Since fissure water is of a different quality than the water in the Wonderfonteinspruit, this has an impact on both quantity and quality of stream water.

Contamination of stream water
In cases where fissure water comes into contact with ore bodies that have been (partly) oxidised because of either mining or dewatering, such water might be contaminated with uranium or other toxic heavy metals released from the ore. At some gold mines the discharge of fissure water had to be stopped since it exceeded limits for ionising radiation (radioactivity) set by the National Nuclear Regulator (NNR) (Khoathane, 2003). In addition, such water also often contains elevated

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[4] This, however, only applies to wetlands which had not been already drained for agricultural purposes prior to dewatering.

concentrations of dissolved solids (indicated by increased electrical conductivity) mainly consisting of sulphates that originate from oxidised sulphides.

2.2.2 Discharge of water used in mining processes ('process water')

In some mines abstracted fissure water is partly used in mining processes such as dust suppression and underground blasting, cleaning of equipment, cooling of underground mine workings, drinking-water supply, metallurgical processes, etc. In other mines water for such purposes has to be imported, e.g. by buying it from water service providers such as Rand Water. Water used in mining processes in this report is termed as '*process water*'. Consequences of discharging process water into the Wonderfonteinspruit include:

Increase of sediment loads
Depending on the nature of the process in which the water was used it subsequently may contain significantly elevated concentrations of suspended solids, many of them originating in dust from rock and uranium-bearing ore. At one mine concentrations of suspended solids were such that canals have been blocked by sediment bars formed by settling suspended solids (pers. commun. Stoch, E.J., 2003). To avoid this problem and reduce concentrations of suspended solids, the pumped fissure water is now diverted over a succession of settling ponds before being discharged into a canal system. Despite large amounts settling in canals, much of the suspended material is likely to have reached the stream where it subsequently accumulates in low-flow areas such as wetlands, weir basins and dams. This may contribute to the contamination of sediments sampled in such areas.

Contamination of stream water with dissolved pollutants
The mechanisms described for the possible pollution of fissure water also apply to process water. In addition to this, the use of water in metallurgical and leaching procedures may add considerably more dissolved contaminants to the water (Pulles, 1991; Pulles et al., 1996).

Contamination of groundwater with dissolved pollutants and suspended solids
Apart from being discharged into streams, in the upper Wonderfonteinspruit abstracted groundwater is discharged via a borehole directly into an adjacent (not dewatered) aquifer. Depending on the quality of the discharged water, this may have an adverse impact on groundwater quality in receiving compartments.

2.3 Impacts associated with uncontrolled release of water from diffuse sources

Uncontrolled release of water from diffuse, mining-related sources into the environment includes, *inter alia*:

- *Porewater-fed seepage* from fine-grained, unlined mining residues such as slimes dams and sand dumps (active and decommissioned) ─ often highly contaminated ─ (Matic & Mrost, 1964), affecting shallow and deep groundwater, as well as surface water such as dams, lakes and streams

- *Run-off* from coarse-grained, unlined mining residues such as ore piles and rock dumps

- *Run-off* from sidewalls of fine-grained mining residues such as slimes dams and sand dumps
- *Seepage* from evaporation facilities (pans, dams)
- *Run-off* and *seepage* from irrigation of vegetated slimes dams with process water
- *Leakages* from unlined dams, canals, pipelines
- *Spillages* of slurry (slimes-water mixture), process water of metallurgical plants, sewerage, etc.
- *Rainwater* not captured in storm-water drainage systems and contributing to run-off from mining property
- *Seepage* from slimes dams

Owing to their large surface area and content of contaminants, slimes dams are likely to be the single largest source of diffuse water pollution by mining. Seepage from slimes dams frequently displays significantly elevated concentrations of uranium and other toxic heavy metals, as well as dissolved salts such as sulphates and chlorides, often severely limiting the usability of affected water resources. In tailings where sulphide oxidation leads to the formation of sulphuric acid (a process termed ‘Acid Mine Drainage’, AMD) the high acidity of the seepage (pH <2–3) is known to aid the liberation of toxic metals from tailings particles. Largely unexplored, however, is the contribution of nitrate and carbon as decay products of cyanides (used as leaching agent for gold), which may promote eutrophication in receiving surface waters.

Owing to large surface areas and volumes, slimes dams generate comparatively large volumes of seepage. Amongst others, seepage release is indicated by spontaneous formation of wetlands at the basis (foot) of many slimes dams. Driven by an elevated porewater head inside the tailings (phreatic surface), a continuous outflow of seepage permanently elevates the adjacent groundwater tables and allows for wetland vegetation such as reeds to grow throughout the year, even during the dry winter season. Comparative studies of tailings deposits under different climatic conditions suggest that seepage losses from decommissioned tailings deposits were in the order of mean annual rainfall volumes they received (Winde, 2003). In most slimes dams eventually a hydraulic equilibrium between infiltrating rainwater and seepage losses will be established at a mean water content of 10–30 wt% (semi-arid conditions of SA). At active slimes dams, however, where additional water from slurry is applied, seepage losses may exceed the MAP by up to several times (Winde, 2003).

Seepage from slimes dams often migrates along hydraulic gradients across shallow aquifers of adjacent floodplain sediments into nearby streams. In small catchments, where a comparatively high proportion of the total area is covered by tailings deposits, such seepage may form a significant proportion of stream flow, considerably reducing water quality (Winde, 2002). Acid mine drainage in tailings often increases the leaching rate for uranium and other heavy metals by orders of magnitude resulting in concentrations of dissolved uranium in the region reaching several hundred mg/l (Mrost and Lloyd, 1970; Winde, 2002). Compared with the discharge-unweighted mean of global background concentration for uranium in fresh water of 0,0003 mg/l (DWAF, 1996), uranium concentrations in seepage are usually between a *thousand to a million* times higher and therefore likely to exceed the natural background of many of the receiving watercourses in mining areas by several orders of magnitude, i.e. in order to dilute the uranium concentration of such seepage to background levels, uncontaminated fresh water of a thousand to a million times the volume of the seepage would be needed. Taking this water needed for dilution into account, the total water use of mining in SA would be considerably higher than the currently estimated 3 per cent of the total water use of the country (DWAF, 2002).

With about a quarter of all South African gold ore milled, processed and deposited by mines of the West Rand and the Far West Rand (Wymer, 1999), slimes dams in this region are assumed also to comprise about a quarter of all gold tailings produced in the Witwatersrand basin (Robb and Robb, 1999). While the total area covered by slimes deposits is estimated to be approximately 400 km^2 (Robb and Robb, 1999), a conservative (under)estimate of some 40 km^2 is used for the Wonderfonteinspruit catchment (Marsden, 1986; GSG, 2002). Using this surface are and an again underestimated mean annual precipitation (MAP) of some 600 mm/a throughout the whole area, slimes dams of the West Rand and Far West Rand receive approximately 24 million m^3 of rainwater per year. The proportion of rainwater infiltrating into tailings (resulting in *seepage’*) largely determines the resulting volume of seepage from slimes dams. The rate at which seepage percolates through slimes dams may vary considerably according to climatic conditions (evaporation rates, rain intensity, etc.) and tailings-related factors such as grain-size distribution, vegetation state, extent of erosion, density and width of cracks in dried tailings, etc. However, with the usually flat tops of most slimes dams having almost no gravitational surface run-off, cracks allowing for easy infiltration of rainwater into deeper layers of slimes, and almost no losses by interception or transpiration from vegetation, the recharge rate on slimes dams is likely to be significantly higher than under natural conditions. While 100 per cent relative air humidity entirely prevents evaporation during rainfall, after rain events much of the infiltrated water is largely protected from evaporation by overlying tailings. Furthermore, many of the slimes dams in the area of investigation are still active and receive additional water input. In view of this and the above-mentioned finding that seepage losses from tailings deposits are in the order of received rainwater volumes, an average applicable seepage-recharge rate of 100 per cent MAP seems to be reasonable. Being possibly too high for decommissioned slimes dams and too low for active ones, it represents a (conservatively overestimated) first-order approximation. Based on this, a total volume of (undiluted) seepage of some 24 million m^3/a (760 l/s) from all slimes dams located inside the Wonderfonteinspruit catchment is to be expected. This equals about the current total surface run-off from almost the entire catchment area of the Wonderfonteinspruit as measured at station C2H069 (measurement period: 10/1997–03/1999).

Assuming an average uranium concentration in tailings seepage of 1 mg/l[5], about *24 t of uranium per year* is transported in dissolved form from slimes dams into ground- and surface water of the Wonderfonteinspruit system.

In addition to the transport of leached contaminants from slimes dams, gully erosion of sidewalls of slimes dams frequently also transports tailings material directly into adjacent watercourses. Being exposed to atmospheric oxygen, bacterial-aided pyrite oxidation in such slimes is not impeded by restricted airflow into deeper layers, as this is the limiting factor for AMD to occur in slimes dams (Mrost and Loyd, 1970). Therefore, oxidation of sulphides readily occurs in such spills, liberating contaminants such as uranium more easily.

Currently, less than 1 000 t of uranium is produced annually by South Africa (Venter, 2001). Compared with 1980, when some 7 200 t of uranium (Harding quoted in Venter, 2001) were extracted, this results in some 6 000 t of uranium per year which are additionally disposed of onto slimes dams (Winde and de Villiers, 2002a/b). Since leaching with sulphuric acid extracted some 90 per cent of the original uranium content from the ore, a tenfold increase of uranium concentrations is to be expected in all tailings which are no longer leached for the radioactive metal. Particularly high concentrations are therefore likely to be found in upper layers of slimes dams at gold mines with above-average uranium grades which have abandoned uranium production.

Along with some 1,1 billion t of gold ore that was milled by mines in the West Rand and Far West Rand up to 1998, more than 150 000 t of uranium were brought to the surface. With only a quarter of it being extracted and sold, the majority of the mined uranium remains in tailings. The slimes dams of the West Rand and Far West Rand contain a total of well above ***100 000 t*** of uranium (1998), reaching *average* concentrations in some mines of over 300 mg/kg. The mass-weighted mean uranium concentration in all tailings of about 100 mg/kg is about two orders of magnitude above the natural background in soils and surface rocks of the area, rendering slimes dams a potential source of uranium contamination (Wymer, 1999).

2.3.1 Other diffuse sources of uncontrolled release of water

In addition to mining residues dumped on the surface, other mining-related sources of diffuse and uncontrolled release of water into the environment exist, including:

- Stormwater run-off from sealed areas such as roads, parking areas, roofs, plants, ore piles and rock dumps which is not collected in stormwater drainage systems;

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[5] This is based on an average retention factor [= U-conc. solids : U-conc. water) of 100 and an average Unat-concentration of 100 mg/kg found in South African slimes dams. The resulting Unat-concentrations in seepage is conservatively underestimated since concentrations as high as 30–>100 mg Unat/l were observed (Mrost and Loyd, 1970; Winde and de Villiers, 2002).

- Spillages of process water;
- Leakages from defect pipelines and broken channels;
- Seepage from unlined return-water dams, evaporation facilities and other water reservoirs such as pollution-control dams, etc;
- Leakages from water supply and waste-water reticulation systems, often exacerbated by mining-induced seismicity and ground instability in the region.

2.3.2 Controlled release of waste water from point sources

Point sources via which uranium-contaminated waste water might be discharged into the Wonderfonteinspruit include:

Domestic waste water from mining-related sewage works
With workforces of gold mines in the order of tens of thousands of people, the resulting sewage volumes are often comparable with those of many medium-sized towns in the area. The treated waste water mainly originates from imported tap water bought from a water service provider such as ‘Rand Water’. At some mines fissure water is treated in water-purification plants and also used for human consumption. Higher uranium concentrations in such waste water are to be expected in cases where miners drink uranium-contaminated water, such as cooling water in underground mine workings, resulting in elevated uranium concentration of the urine, as detected in some cases (Steenkamp, 1996).

Process water from metallurgical gold/uranium plants
Although much of the water in metallurgical plants is recycled and reused, some of the water needs to be discharged. Based on a volume of 2 000 l/s of mine-water effluent with an average uranium concentration of 0,74 mg/l (Pulles, 1991)[6], gold mines in South Africa discharge a total of approximately 50 t of uranium per annum into adjacent streams. Based on a 25-per cent share of the West Rand/Far West Rand area on the total gold mining output, it can be assumed that mines in the area discharged about 12 t uranium per year into fluvial systems. Since uranium concentrations in process water of uranium plants are generally higher than in gold plants, owing to the leaching of uranium from the ore, it is likely that even higher uranium loads occur in the Far West Rand considering the higher number of uranium plants in the area. With the decrease of uranium production this source of stream contamination has become less important. However, the associated positive effect of decreasing uranium production might be counterbalanced by the afore-mentioned increase of uranium concentration in slimes dams.

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[6] This concentration is approximately ten times the current South African guideline level for ideal drinking water, more than 70 times the tentative South African guideline level for irrigation and is more than 30 times the level for drinking water determined in Section 9.7.5 (Regulatory limits)

Surface run-off from stormwater-drainage systems

Stormwater-drainage systems collect mainly rainwater run-off from sealed surfaces such as tarred roads, concrete-covered areas and roofs. Owing to much higher run-off coefficients this can result in almost 100 per cent of the rainwater from such areas flushing untreated into nearby streams. Containing a wide range of heavy metals such as Pb (originates in petrol), Cd (abrasion of tyres), Zn and Cr (corrosion of cars, gutters, roof material), run-off from roads and other sealed surfaces constitutes a significant source of stream contamination (Winde, 1996).

In addition, fine windblown-dust from adjacent slimes dams is frequently flushed into stormwater-drainage systems. Concentrating dust from large surface areas in comparably small drainage channels often results in outlets of stormwater-drainage systems being a significant point source for discharging contaminated sediments into streams (Winde, 1996). Assuming for the whole Wonderfonteinspruit catchment a total area of some 50 km^2 of sealed surface in the vicinity of slimes dams on which in the course of a year a dust layer of only 1-mm thickness is deposited and entirely flushed into the stormwater- drainage system, a sediment load of approximately 100 000 t/a would result. With slimes material containing on average 100 mg/kg uranium, stormwater-drainage systems discharge about ***10 t uranium*** *per year* into nearby streams. This is about the same amount of uranium that the Wonderfonteinspruit received in dissolved form from point sources (mine effluents) and that is released via seepage from slimes dams respectively. While 50 km^2 might be slightly overestimated, the assumed thickness of 1 mm dust deposited over a whole year is certainly too little, considering that dust concentrations of up to 3 700 mg per m^3 of air were reported from areas adjacent to slimes dams of the East Rand during a windy day. With an average density of dry slimes of about 1,8 g/cm^3 (less than the density of a single particle due to the pore space remaining between compacted spherical particles) a single event with such dust concentration already results in a layer of slimes dust of about 2 mm thickness. Even without having exact numbers for the Wonderfonteinspruit catchment, this illustrates that stormwater-drainage systems may constitute an important source of uranium pollution.

Other sources likely to contribute to the contamination of stormwater with uranium include run-off from ore piles, and rock and sand dumps, as well as from uranium plants where possible spillages of process water, dust and uranium concentrate may be found. Furthermore, tailings particles eroded from nearby slimes dams may be transported into stormwater-drainage canals. Rainstorms exceeding an intensity of a 1 in 50a will in most cases result in additional spills of run-off from slimes dams overflowing the prescribed 0,8-m high free board of stormwater-retention dams.

There are also reports about illegal use of stormwater-drainage channels to dispose of highly contaminated process water from metallurgical plants in the upper part of the catchment (Parker, 1982).

2.3.3 *Accelerating karst-related ground movements*

Owing to the lowering of the groundwater table accelerated formations of sinkholes, dolines and ground subsidences were observed. Consequences for water resources include:

- Creating potential sources of off-site contamination by filling formed sinkholes for stability reasons with tailings from gold mines. Findings of a recent study into the effects of tailings-infilled sinkholes on groundwater quality suggest that they act as significant sources of uranium contamination (Dill and James, 2003).
- Frequent breaches of water and waste-water reticulation systems, with increased water losses through leaking pipelines and water contamination by waste water (pers. commun. Swart, C.J.N., 2003)
- Depreciation of commercial land value (pers. commun. Stoch, E.J., 2003)
- Creation of further sources of pollution (including bacteriological) by misusing sinkholes as illegal waste dumping sites (Dill & James, 2003)
- Further reduction of the surface run-off and increase of groundwater recharge through sinkholes.

2.3.4 *Diverting stream flow into a pipeline*

In order to avoid that pumped fissure water from underground recharges backs into the underground mine workings through sinkholes, which preferentially formed in the vicinity of the stream channel, the Wonderfonteinspruit was completely diverted into a 26-km-long pipeline (equals >20% of total length of the Wonderfonteinspruit). Consisting of rubber-lined steel with a diameter of 1 m, this pipeline more or less follows the course of the (now dry) stream channel. Some of the consequences for flow and quality of water associated with the diversion of stream into this pipeline include:

- Confining stream water to a pipe, and thereby preventing interactions with the natural environment such as the atmosphere, sediments, aquatic ecosystems, etc. directly or indirectly affects the self-purification capacity of the stream. Mechanisms affected include sunlight-dependent biological decalcification and associated pH-fluctuations that trigger precipitation of dissolved metals, flocculation processes due to microbiological activity, etc., in about a third of the total length of the stream.
- The pipeline also prevents dilution of contaminant concentrations in the stream water by excluding groundwater and surface run-off.
- The above factors allow for extended transport distances of pathogenic bacteria and other pollutants originating from raw-sewage inflow, with the latter being frequently observed at Donaldson Dam as starting point of the pipeline.

- The complete diversion of stream flow into the pipeline exposes (supposedly) contaminated stream sediments of the dry streambed to oxygen and the associated liberation of contaminants such as uranium and other heavy metals.
- Since no areas of low flow velocity, as e.g. in wetlands, occur inside the pipeline, rates of downstream transport of sediments are likely to increase.
- Water-dependent riparian ecosystems such as wetlands, benthic, aquatic and riparian habitats, etc. were largely destroyed.
- The reduced potential of the altered streambed to reduce peak-flow volumes and retain sediments is of particular concern during storm events, which may lead to floods flushing down the stream channel.
- The diversion of the stream flow also reduced the water availability for inhabitants and fauna of the riverbanks.
- In addition it may also affect the microclimate and aesthetic value of the scenery.

2.3.5 Internal use of fissure water by the mines

Some mines increasingly use fissure water for mining purposes such as transport and deposition of tailings, irrigation of slimes dams, leaching processes, cooling underground mine working, etc. Consequences of doing so include:

- Reduction of the volume of water available for downstream users and the environment.
- Reduced dilution of pollution loads from upstream of the point of discharge.
- Some of the water may partly flow back into the system as return flow from diffuse sources such as slimes dams ─ then, however, often considerably contaminated.

2.3.6 Import of water from areas outside the catchment via water service providers

Owing to its good quality, imported water is likely to have an overall positive effect on the quality of water resources in the Wonderfonteinspruit catchment, mainly because of dilution of pollutants in receiving water bodies of the catchment. Therefore, reducing the import of such water ─ e.g. by using fissure water ─ will most likely result in an overall increase of contaminant concentrations in receiving watercourses.

2.4 Impacts associated with the altering of run-off coefficients of occupied surface areas

As a result of reduced borehole-water availability for agricultural usage and of mining-induced establishment of settlements, roads and mining infrastructure such as hostels, shafts, metallurgical plants, parking areas, etc., the land-use patterns in the Wonderfonteinspruit catchment have changed considerably over time after mining commenced in the area. Some of the associated consequences for surface and groundwater resources are listed below.

- Changing land-use patterns on mine lease areas often alter the proportion of rainwater that runs off and infiltrates into soil respectively (run-off coefficient). While some activities such as sealing surfaces with tarred roads and buildings, and increasing topographic gradients in the microrelief by erecting prominent structures such as tailings dams, rock and sand dumps, etc. increase run-off coefficients, other activities such as vegetating formerly bare ground and creating trenches, pits, etc. may have the opposite effect.

- Run-off coefficients of sealed surfaces such as tarred roads, concrete-covered areas around metallurgical plants, offices, hostels, residential areas, and the buildings and roofs themselves are significantly higher than those of unsealed (natural) surfaces such as open grassland, soil, lawns, etc. Thus run-off from mine lease areas in general is artificially elevated compared with natural (premining) conditions. Together with the pollution of such run-off, this leads to an overall increase of waste-water discharges and a decrease of natural groundwater recharge.

- In cases where drained stormwater reaches the (now dry) Wonderfonteinspruit, traversing dewatered compartments, an increased recharge of groundwater via sinkholes may occur, especially since sinkholes are particularly concentrated in the streambed. The associated increase in groundwater recharge is likely to increase the ingress of fissure water into underground mine workings.

- The deposition of tailings in SD up to several tens of metres above ground creates artificial hydraulic gradients between phreatic surfaces developing inside the deposits and adjacent groundwater tables. This again drives seepage from slimes dams into groundwater and adjacent streams. Such seepage frequently displays concentrations of sulfate, heavy metals, uranium and CN-borne nitrogen and carbon that are significantly above natural background levels.

2.5 Other (indirect) mining-related impacts

- Illegal leaching of stolen auriferous slimes material, with highly toxic mercury (Hg) (amalgamation), being flushed into nearby streams may contribute to water contamination.

- Contaminants from discharged fissure water frequently accumulate in sediments of affected streams, often reaching higher concentrations than in the actual source of contamination.

- Such sediments may temporarily release accumulated contaminants, constituting secondary sources of contamination.

2.6 Impacts associated with the rewatering of formerly dewatered aquifers

Rewatering refers to the natural process of replenishing formerly dewatered aquifers by rain and stream water after pumping of fissure water from underground mine workings has ceased. Although rewatering ─ in the true sense of the word ─ occurs as soon as natural recharge exceeds pumping rates, the term is commonly used only to refer to increasing groundwater levels once mining-related pumping has stopped completely. Associated impacts on water quantity and quality include the following aspects, which are of particular concern:

2.6.1 *Cessation of pumping fissure water into the Wonderfonteinspruit*

The cessation of pumping after mine closure implies that fissure water will no longer be discharged into the Wonderfonteinspruit. Being currently the most significant contribution to stream flow, this will significantly reduce volumes available to downstream users such as the city of Potchefstroom which relies entirely on surface water. This is exacerbated by the fact that, apart from fissure water, discharge of purified waste water from mining-related sewage works that mainly originates from imported water will eventually also stop. In addition, large proportions of rainfall on surface areas of dewatered compartments and of stream flow entering the latter from upstream will only contribute to groundwater recharge. Until premining water levels are reinstated in the formerly dewatered compartments most of the water entering this area will not be available for downstream users. This situation may last up to several decades, depending on recharge rates and groundwater losses to downstream compartments via mined-through dykes (Dill and James, 2003). Possible consequences of such an extended dry period in the Wonderfonteinspruit due to rewatering include:

- Water-shortages for users dependent on pumped mine water such as farmers and the City of Potchefstroom
- A severe reduction of stream flow downstream of former discharge points will have an adverse impact on aquatic ecosystems such as wetlands, etc. ('ecol. reserve')
- Insufficient dilution of pollutant inputs from municipal sewage works that will continue to discharge waste water into the Wonderfonteinspruit. This may cause deterioration of water quality with particularly high concentrations of contaminants occurring during low-flow conditions in dry seasons.
- Change of flow regime of the lower part of the Wonderfonteinspruit from perennial to only seasonal or even episodic.
- Prolonged exposure of uranium-contaminated sediments in wetlands, dams and the stream channel to atmospheric oxygen during dry times
- Reduction of total uranium load if fissure water was the main source of uranium input.

2.6.2 *Increasing water levels in formerly dewatered compartments*

After the cessation of pumping, groundwater will finally fill the underground mine voids and overlying aquifers. Currently it is still uncertain how long the rewatering process will take and whether premining groundwater levels can be restored at all in the dewatered compartments. The two main models addressing the latter question and their associated consequences are briefly outlined below.

'Megacompartment' model

Since formerly impermeable dykes which separated the groundwater compartments from each other have been mined through, at least three of the dewatered compartments are now hydraulically interlinked, forming a so-called 'megacompartment'. This allows for water to flow downstream through the pierced dykes (Venterspost D. and Bank D.) from the two upstream-lying compartments (Venterspost C. and Bank C.) into the lowest-lying compartment (Oberholzer C.). With the downstream dyke of the receiving compartment still being impermeable (not mined through), groundwater there will rise until it reaches the surface and decants via a reactivated spring ('Oberholzer eye') into the Wonderfonteinspruit. Assuming an unlimited water flow between the compartments, the water tables in all three compartments will be at the same level, with the highest possible elevation at the level of the spring as ultimate point of decant. If this scenario applies, final groundwater tables in the two upstream departments would remain far below pre-mining levels (up to 60 m in the upper part of the Bank and Venterspost compartments).

Consequences of this scenario include:

- Former springs on the upstream sides of the dykes in both 'upstream compartments' will not flow again, and will thus not contribute to stream flow

- A large part of the Wonderfonteinspruit stream channel (ca. 20–25 km) would remain dry, with all afore-mentioned impacts on aquatic ecosystems, local users, microclimate, habitats and fluvial dynamics of stream flow and sediments

- After complete rewatering the discharge of the spring in the lowest-lying, hydraulically connected compartment will significantly exceed premining flow rates, then discharging about the sum of the premining flow of all springs in the upstream compartments

"Permeability gradient" model

In contrast to this Dill and James (2003) first suggested that drastically decreasing permeability of rocks underneath the karstic zone of the dolomite would not allow for sufficient water flow into underground mine workings and through perforated dykes, rendering it unlikely that a common water level in all three rewatered compartments would finally be established. The authors assume that the natural recharge will exceed water losses from the karstic zone to the deeper underground and that, therefore, the upper (cavernous) zone of the dolomite will gradually be filled by infiltrating rainwater, finally reaching premining groundwater levels. In contrast to predictions of the 'mega-compartment model', this implies that springs in all three compartments will flow again. However, owing to water losses to the lowest compartment the spring flow in upstream compartments will be below premining levels and therefore more prone to cease during longer dry spells. The water lost at the upstream compartments will increase the flow of springs in the lowest-lying compartment. Depending on which of these two scenarios eventually will materialize, different consequences for water flow and quality will result. Some of the aspects associated with the different scenarios are outlined below.

2.6.3 Ground-stability aspects

Since the formation of sinkholes, dolines and ground subsidence significantly increased soon after dewatering commenced, and the lowering water table moved through the cavernous zone of the upper dolomite, predictions are that this will re-occur as soon as the rising water table reaches that zone again. Mechanisms discussed in this regard include increasing sheer stress at end points of remaining arches of chert bands that span large cavities, decreasing support of such structures owing to lack of buoyancy, and subsurface erosion of fill material in palaeosinkholes by infiltrating rainwater migrating across the cavernous dolomite. It was also suspected that increased volumes of pumped groundwater discharged into the Wonderfonteinspruit may have contributed to the accelerated development of sinkholes inside the stream channel of the Wonderfonteinspruit (Enslin, 1951; Brink, 1979). In how far re-established buoyancy, after a complete refilling of the karst system and the associated reduction of vertical water flow through the cavernous zone, will assist long-term consolidation still needs to be determined.

In places where near-surface groundwater levels are to be re-established this might lead to basement instability of waste dumps, houses and any other structures built in low-lying areas on previously dry ground during the decades of dewatering.

In case predictions where the ‘megacompartment model’ applies, groundwater tables in rewatered compartments will remain up to several tens of metres below their premining levels, fluctuating within the cavernous zone of the dolomite. The ongoing movement of water through this highly permeable zone, associated with seasonal fluctuations of the groundwater table, is likely to increase further karstification and collapses of cavities, as the weathered part of the dolomite is most vulnerable to phreatic solution and subsurface erosion. Downstream of the lowest-lying spring, increased stream flow may contribute to fluvial erosion, particularly at inlet caves and swallow holes (‘ponors’) at the bottom of the stream channel and in subsurface channels inside the dolomite.

In addition to karst-related effects, the replenishment of dewatered compartments is also associated with the build-up of a water column, up to several thousands of metres high, that exerts additional pressure on abandoned underground mine voids. At present no information could be obtained on whether or not this might have negative implications for the long-term stability of (artificially) plugged water conduits (as found e.g. at West-Driefontein) and underground mine workings that may collapse (although buoyancy might mitigate the effects of water pressure).

Similar to the effects of large dams, which often trigger seismic movements owing to adjustments of the geological underground after being filled, rewatering also may lead to short-term increases of seismicity because of an adjusting geological environment considerably altered over decades of mining.

The question as to how far possibly elevated acidity of groundwater from underground mine workings due to Acid Mine Drainage (AMD) may accelerate the dissolution of dolomitic carbonates, and therefore increase chemical weathering and associated consequences such as occurrence of sinkholes, dolines and ground subsidence, should also be included in future investigations addressing stability-related aspects of rewatering.

Water-availability aspects

After a slow initial phase in which the mine voids, extending several thousands of metres below surface, will be flooded, groundwater levels are expected to rise much quicker once they reach overlying rock formations with a comparatively low storativity (0,01%). The increase of groundwater levels will again slow down once the cavernous upper zone of the dolomite about 100–200 m below surface is reached. where large karst systems in the form of interlinked caves, dissolution slots and joints need to be filled before groundwater tables can reach the surface. In this weathered zone of the dolomite, with an average storativity of about 10 per cent, the groundwater increase will be about 1 000 times slower than in the underlying bedrock. It is therefore estimated that it may take several decades after cessation of mining-related groundwater pumping before premining water levels are re-established and groundwater via reactivated springs and base flow will contribute to ***stream flow*** in the Wonderfonteinspruit again (Swart et al., 2003). During this time availability of naturally occurring water in the area will be severely reduced.

Whether groundwater tables ultimately will be re-established at their premining levels depends mainly on the volumes of groundwater lost to the lowest-lying compartment through cross-compartmental flow via underlying bedrock and mined-through dykes[7]. If such cross-compartmental water flow through pierced dykes (eastward) can be avoided (e.g. by sealing mined-through dykes with plugs), original flow rates may be reached again at the affected spring. If complete sealing cannot be achieved and the '*megacompartment model*' assumptions apply, premining groundwater levels will not be reached in the compartments upstream of the lowest-lying compartment. Consequences of this include:

- The resulting groundwater tables in the two upstream compartments will be between 30 and 90 m below their original levels, increasing with growing distance from the downstream compartment ─ i.e. in many areas of those compartments boreholes of farmers will remain dry.

- The dolomitic springs of the upstream compartments will remain dry.

- Stream flow will be markedly reduced and confined to rain events (episodically) since no base flow by dolomitic springs will be provided.

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[7] Possible losses of groundwater to compartments in adjacent catchments not considered

- Surface water-reliant users and ecosystems will have no access to water; wetlands in this area are likely to remain dry, not being able to buffer flood peaks in flow and retain pollutants from upstream.

If the ‘permeability gradient model’ applies, original (premining) groundwater levels eventually will be re-established and, therefore, springs will flow again. Consequences of this model would include:

- Losses of groundwater through dykes to the lowest-lying compartment will reduce flow rates at upstream springs, rendering them more prone to fall dry during longer dry spells. This, in turn, would result in less constant stream flow in those compartments and might turn the flow regime of the Wonderfonteinspruit from perennial into seasonal, simultaneously reducing the stream’s capacity to dilute waste-water discharges, e.g. by municipal sewage works.

- The flow rate of the lowest-lying spring in the downstream (receiving) compartment is likely to increase. This increase will be about equivalent to the flow decrease of the upstream-lying springs.

- Increasing water levels may also accelerate ***cross-compartmental outflow of water*** to compartments bordering to the west, north and south via pathways such as mine workings, stopes, blasting-induced fractures, boreholes, pipes, etc. This again might reduce the flow rate of the lowest-lying spring of the dewatered compartment.

- Owing to the increased number of sinkholes the surface run-off will be reduced in favour of increased groundwater recharge rates.

- Seepage from slimes dams may provide seasonally stable base flow to shallow (perched) aquifers feeding into the Wonderfonteinspruit. This is particularly applicable to the upper non-dolomitic part of the catchment where:

    - Losses to deeper aquifers are smaller than in dolomitic areas (quartzitic bedrock of low permeability).

    - The proportion of slimes dams-covered areas of the total catchment is higher than downstream.

    - Slimes dams are generally situated closer to the stream.

    - The topographic gradients of the headwater region are generally steeper, allowing for higher proportions of interflow after rainfall than in the undulated downstream parts of the Wonderfonteinspruit catchment.

    Under such conditions the water quality of the stream can deteriorate significantly.

2.6.4 Water-quality aspects

Stream contamination in the headwater region

The problem of low dilution of tailings seepage in mining-affected headwater regions of streams is illustrated by the fact that long-term average EC-values of stream water in the upper Wonderfonteinspruit (DWAF, HIS data for station C2H152, 1971–2000) are almost twice as high as in the lower Wonderfonteinspruit, despite the latter having received waste effluents from almost the entire catchment (DWAF station HIS data for station C2H069).

The situation is likely to worsen during dry winter times when seepage from slimes dams is almost the only source of base flow feeding the stream. Findings from the headwater region of the Natalspruit near Alberton (Central Rand goldfield) suggest that about a quarter of the total flow measured in March 1999 (after an above-average wet summer) originated in seepage from adjacent tailings. The proportion of seepage to the total flow coincided with the proportion of the total catchment area covered by mining residues such as mine dumps and slimes dams (Winde and de Villiers, 2002). Apart from elevated levels of EC (as a synonym for the concentration of dissolved salt), under such conditions high concentrations of other tailings-related contaminants in the stream water such as uranium are also likely to occur. In the case of the upper Natalspruit this resulted in an extrapolated annual load of dissolved uranium of some 400 kg. It is likely that such factors have contributed to the extremely high uranium concentration of 4 mg/l found in a grab sample from Russell Stream (Central Rand, Johannesburg) without continuous monitoring (Kempster et al., 1996). With many slimes dams in the headwater region of the Wonderfonteinspruit being abandoned, and many of them heavily eroded and subject to extensive acid mine drainage, such extremely high uranium concentrations are not unlikely to occur in the upper Wonderfonteinspruit as well.

Groundwater contamination by tailings-filled sinkholes

Since large-scale dewatering commenced about 1 000 sinkholes may have occurred in the affected region (pers. commun. Swart, C.J.N., Ground Stability Group Gold Fields Ltd, 2003). To increase stability of adjacent areas and decrease associated risks for local residents, many of the sinkholes were filled with slimes material from tailings dams, simultaneously reducing possible groundwater recharge through such conduits (Swart et al., 2003; Dill and James, 2003). In cases where sinkholes occurred near or underneath existing slimes dams, fresh slimes from the metallurgical plant were pumped from the pipeline directly into the cavities. In some instances it took several months of ongoing pumping slimes until such cavities were filled (pers. Commun Stoch, E.J., Environmental Consultant Welverdiend, .2003).

Where rising groundwater tables submerge such *filled* ***sinkholes,*** contaminants such as uranium might be leached from the tailings material and transported downstream. In cases where AMD occurs, the leaching of heavy metals including uranium will be enhanced, simultaneously increasing the salt load (EC) and acidity (lowering pH) of the groundwater. This is supported by data from a leaching experiment and chemical modeling predicting uranium concentrations in seepage from filled sinkholes of 0,3 mg/l and 60–310 mg/l respectively (Dill and James, 2003). Considering that only slimes material with a well-below average uranium concentration was investigated (15–45 mg/ kg, while the mass-weighted average uranium concentration of slimes in this area is 119 mg/kg), and owing to some peculiarities of the applied methodology, these values (especially the lower range) are likely to underestimate the associated uranium contamination (Winde, 2003: Comments on the methodology used in Dill and James 2003, unpublished, 8 pp).

Groundwater contamination in underground mine workings

Water in contact with oxidised ore bodies in ***underground mine workings*** is likely to be contaminated by uranium that is liberated from minerals such as uraninite (UO_2) and pitchblende (U_3O_8) ─ the most common uranium-bearing minerals in the mined gold reefs of the Far West Rand ─ both unstable in the presence of free oxygen. A question arising from this is whether this process will fade out once the mine void is flooded and no free (gaseous) oxygen is available.

For long-term predictions of spring-water quality it is also important to understand the groundwater flow after the compartments have been completely rewatered. Of particular interest in this regard is whether contaminated water from the filled mine void will be rather stagnant once the compartment is filled, resulting in different consequences for the quality of ground- and surface water.

2.6.5 Groundwater hydrodynamics

In the case of groundwater in underground mine workings being more stagnant, it is assumed that infiltrating 'clean' rainwater in the highly permeable cavernous zone of the upper dolomite will be the only mobile element of the groundwater entirely feeding the dolomitic springs (pers. commun. Stoch, E.J., 2003). Being stagnant in the mine void and separated from the cavernous zone of the dolomite by several thousand metre of rock with low permeability, it is assumed that the contaminated water from underground mine workings will therefore be topped by a layer of clean water with which only very limited interactions, if any, take place. Therefore the quality of spring water will generally be good, only impeded by possible seepage from slimes dams that may migrate via shallow (alluvial) aquifers into the fluvial system.

U-tube effect

It is, however, also possible that former shafts act as conduits for vertical water flow through rocks of otherwise low permeability. Being laterally connected underground by mine workings this may result in the so-called ***'U-tube effect***', where water is assumed to flow downwards to the flooded underground mine workings in one shaft and to cross over through filled mine voids to other lower-lying shafts. Driven by hydraulic gradients, resulting from such differences in elevation, water might flow upwards inside the receiving shafts and reach the surface. In that case dissolved contaminants from oxidised rocks and ores in the mine void will finally reach the stream. The resulting groundwater quality is mainly determined by the ratio between the influx of clean (uncontaminated) rainwater and the rate of contaminant release from the ore body into this water. Should AMD decrease once the mine void is filled, a gradual improvement of the water quality is to be expected. If, in contrast, infiltrating rainwater keeps on dissolving contaminants from the rock face ground and stream pollution will remain a long-term problem. The 'U-tube effect' can occur in a single compartment, as well as across boundaries of compartments which are hydraulically interlinked, e.g. by mining through the separating dykes.

Gradient flow

While the U-tube effect would result in a rather quick groundwater flow through mining-related conduits that offer no flow resistance, plugging (sealing) of shafts and underground mine workings could supposedly minimise such flow. It is, however, rather unlikely that water in mine voids will remain totally stagnant given the high number of fissures and faults in this tectonically stressed area, providing pathways for flowing water. This would result in contaminated groundwater from the mine void eventually reporting to the surface at the lowest point of the compartment ('megacompartment' respectively). Since such flow only occurs once the compartment is filled, the surfacing of contaminated water from the mine void may only occur several decades after completion (not start) of rewatering.

Thermal convection

Apart from hydraulically driven water flow along preferential pathways, mixing processes between shallow and deeper groundwater due to thermal gradients along the water column, several thousands of metre high, might also occur. With deep groundwater at 1–4-km depths below surface being significantly warmer than shallower groundwater, due to rock temperatures rising with increasing depths ('geothermal gradient'), convection-driven mixing of groundwater from underground workings with the overlying water column may occur. This would allow for contaminants to enter shallow groundwater finally polluting spring and stream water as well. If such a convectional mixing process is possible at all, it would occur largely independently from hydraulic conditions.

Stream pollution by contaminated sediments

During a possible phase of rewatering where fissure water is no longer discharged into the stream and stream flow ceases for an extended period of time, existing wetlands may disappear and fluvial ***sediments may fall dry***. Being exposed to oxygen may aid the liberation of uranium and other heavy metals from such sediments in which they are accumulated to partially extreme levels, especially in dams and wetlands. Sporadically occurring run-off after storm events may be contaminated and flush uranium and other heavy metals downstream.

Capillary ascending porewater in such sediments frequently leaves extensive ***crusts of salts*** (sulphates) on the sediment surface after it evaporates. With uranium and other heavy metals being particularly highly enriched (factor 7–10 compared with concentrations in the underlying material) and with a high solubility, such crusts might act as (secondary) sources of pollution for rainwater run-off and episodic stream flow.

Decrease of dilution

If the discharge of ***sewage effluent*** from urban areas and informal settlements is continued through the 'dry' phase of rewatering, the ***lack of dilution*** by uncontaminated water may cause unacceptably high levels of sewage-born pollutants such as bacteria, NH_4, NO_3 and heavy metals typical for urban environments (Pb, Zn, Cd, Cu, Cr).

Impacts of buffer capacity of dolomitic rock

Owing to extended contact time between the replenished groundwater and dolomitic rock (to a lesser extent this applies also to surface water) and the associated dissolution of ***dolomite,*** concentrations of Ca, Mg and CO_3 are likely to increase, resulting in higher pH-values and hardness of ground-, spring and stream water. This may counteract (***buffer) the acidification*** of groundwater by acid mine drainage from mine workings and acidic seepage from slimes dams migrating into subjacent aquifers. It was, however, pointed out that the coverage of dolomite with precipitation products, such as iron hydroxides, may in fact limit the buffer capacity of dolomite to the very first phase of rewatering.

Reactivation of stream flow in formerly dry reaches of the Wonderfonteinspruit

Along with dewatering, sinkhole formation, particular in the stream channel and adjacent areas of the Wonderfonteinspruit, was accelerated to such an extent that a large proportion of the stream water was lost to the dolomitic bedrock via such conduits. Percolating through the dewatered dolomite and finally reaching underground mine workings, the water had to be pumped back to the surface again in the early 1970s, and it was decided to divert the stream from its original channel into a 26-km-long rubber-lined steel pipeline of 1-m diameter traversing the dewatered compartments. During decade-long maintenance of the dewatered status in selected compartments the formation of sinkholes and dolines continued, continuously providing new conduits for occasional stormwater to seep directly into underlying bedrock and further into mine workings. In order to prevent such accelerated recharge of groundwater and to reduce the associated (costly) pumping, many of these sinkholes were filled with tailings material from nearby slimes dams of gold mines. In case the 1-m pipeline is to be removed after completion of rewatering as part of a remediation programme, the following consequences, *inter alia*, should be considered:

Acceleration of subsurface erosion

This may occur in the cavernous zone of the upper dolomite owing to excessive stream- water losses to the underlying karstic system via sinkholes acting as ponors. This is of particular concern in stretches where groundwater levels in the rewatered compartments will not reach premining levels and active fluvial erosion will affect deeper parts of the cavernous zone. Consequences include:

- Further acceleration of ground instability (sinkholes, dolines, ground subsidence).
- Severe reduction of stream flow or even disappearance of the stream downstream of ponors due to losses to the cavernous zone.
- This simultaneously leads to increased flow rates of dolomitic springs upstream of the lower dykes of each affected compartment.

Accelerated erosion of tailings-filled sinkholes

A large proportion of sinkholes that have occurred in the area because of dewatering is located in the vicinity of the stream channel. An evaluation of data in Swart et al., 2002 revealed that around 80 per cent of all reported sinkholes occurred within a 100-m-wide band on both sides of the stream channel of a 26-km-long stretch where the Wonderfonteinspruit traverses dewatered compartments. With about one to two thirds of all sinkholes being filled (pers. communun. Swart, C.J.S., GSG, 2003) (many with tailings material from neighbouring slimes dams), it is likely that many of those filled sinkholes will be subject to fluvial erosion once the stream flow in this stretch of the Wonderfonteinspruit is reinstated. Consequences associated with this may include:

- Reactivation of filled sinkholes, providing new conduits for further groundwater recharge and enhancement of subsurface erosion

- Downstream transport of uranium-bearing tailings from eroded fill material into wetlands and reservoirs

Deterioration of stream-water quality

Uranium may be leached from submerged tailings in sinkholes, particularly by stream water of low pH-values as a consequence of acid rain or upstream base flow contaminated by (acidic) seepage from adjacent slimes dams. If stream water is swallowed and flows mainly underground, calcite precipitation and other sunlight-dependent mechanisms of selfpurification will be reduced. Simultaneously wetland areas will not be reactivated, which also has negative impacts on the water quality. Impacts of waste-water inflows will pollute deeper dolomitic groundwater more easily.

3 Inventory of uranium sources and pathways in the catchment (F. Winde)

In a number of previously conducted studies uranium was identified as a major element of concern in terms of surface and groundwater contamination in the Wonderfonteinspruit catchment (IWQS, 1999; Wade et al., 2002; Coetzee et al., 2002). Uranium mainly originates from mining activities in the catchment which liberate the radioactive heavy metal from the lithosphere and allow for its subsequent migration from mining properties into the environment. This chapter describes possible mining-related sources of uranium and selected pathways along which uranium migrates into aquatic systems of the environment.

3.1 Background

Uranium is a natural constituent of the earth's crust with an average global concentration in soils and rocks of 2–4 mg/kg (Turekian and Wedepohl, 1961; ATSDR, 1999). However, auriferous sediments of the Witwatersrand basin that are mined for their gold contain much higher concentrations of uranium. Depending on the mined reef, uranium concentrations range from several tens of mg/kg in the Evander goldfield and the East Rand to several hundreds of mg/kg in the Far West Rand and the Klerksdorp area. In certain carboniferous reefs (isolated kerogen seams) uranium even reaches up to several thousand ─ 58,000 mg/kg (Cole, 1998). With a mass-weighted mean concentration of about 110 mg/kg uranium across all seven goldfields of the Witwatersrand basin (Wymer, 1999; Winde, 2001), the mined reefs contain 10–100 times more uranium than gold; i.e. for each ton of gold produced, mining simultaneously brings about 10–100 t uranium from the geological underground to the surface, exposing it to a chemically much more aggressive environment.

After a peak in uranium production in 1980, the uranium price on the world market ─ and subsequently uranium production in South Africa ─ steadily declined (Cole, 1998; Ford, 1993). Of the 26 South African gold mines, which at one stage were feeding 18 uranium recovery plants, only three mines and four plants were left by 1994, producing approximately 1 600 t U_3O_8 per year (Cole, 1998). About a third of the total uranium production in SA currently comes from the uranium plant of Western Areas (600 t/a).

While mining effectively removes a certain amount of naturally occurring uranium from the area as a whole by extracting it from the ore and selling it to buyers outside the catchment, it simultaneously increases uranium concentrations in the near-surface biosphere considerably. In addition to the elevation of uranium *concentrations* of up to 300 times above natural background levels, mining also increases the *mobility* of uranium by milling and leaching the mined ore, and exposing it to atmospheric conditions. With free water and oxygen, as well as pronounced temperature fluctuations, the atmosphere constitutes a chemically more aggressive environment than the geological underground from where uraniferous ores were extracted. It is for this reason that uraniferous mining residues deposited on the surface of mining sites such as tailings are often of greater concern for possible uranium contamination of the adjacent environment than the mined reefs as primary uranium source.

Apart from mining residues, oxidised ore bodies in underground mine workings and ore-treatment facilities on the surface, such as crusher plants, metallurgical plants and their associated infrastructure (pipe, canals, etc.) also constitute potential sources of water contamination. While controlled discharge of contaminated mine and rain water into adjacent streams via canals and pipelines, as well as accidental spills of process water into such systems, is termed ‘point-source pollution’, the uncontrolled release of water from mining sites, e.g. through seepage from slimes dams, contaminated rainwater run-off from rock and sand dumps, ore piles and uranium-production areas, as well as seepage from process water dams, evaporation facilities, canals and pipelines, constitute ‘diffuse sources of contamination’. While the former is usually confined to active mines and ceases when mining stops, the latter usually remains of concern long after mine closure.

Once uranium is liberated from rock material and dissolved in water it migrates in solution into receiving water bodies and other environmental components such as soil, air and biota. Being non–biodegradable, uranium as all heavy metals tends to accumulate in the environment, often reaching off-site concentrations in sediments, soils and biological matter that exceed those in the actual source of contamination. Under certain conditions such contaminant reservoirs temporarily release accumulated pollutants and act as ‘secondary sources of contamination’.

3.2 Sources of uranium pollution in the Wonderfonteinspruit catchment

Potential sources of uranium pollution in the Wonderfonteinspruit catchment can be divided into four major categories:

- Uranium sources on gold-mine properties (further referred to as ‘on-site sources’)
- Gold mining-related uranium sources outside mine properties (‘off-site sources’)
- Mining-related uranium accumulations in the environment (secondary enrichments)
- Non-mining-related sources of uranium

3.2.1 Gold mining-related ‘on-site sources’ of uranium

Gold mining-related sources of uranium contamination can be subdivided into point-sources through which contaminated water is discharged in a controlled manner using pipelines, canals, etc., and diffuse sources from which uranium-contaminated effluents are released with no control.

Point sources of uranium contamination include:

- (Fissure) water from underground mine workings that was in contact with oxidised uranium ore
- Water used in mining processes (‘process water’) from operations underground (for dust suppression, etc.) and on surface, e.g. in metallurgical plants (leaching ore, floatation) and transportation of tailings (slurry, return water)

- Stormwater run-off from contaminated areas such as ore piles, gold and uranium plants, tailings dams (sidewalls), rock dumps, sand dumps, tailings-dust-covered sealed surfaces near slimes dams and various types of retention dams
- Sewage effluent with elevated uranium levels in urine from hostels of underground mine workers (Pulles, 1991, Anonymous, 1990, Slabbert, 1996)

Diffuse sources from which uranium-contaminated water is released from mine lease areas into the environment in an uncontrolled manner include:

- Seepage from active (unlined) slimes dams
- Seepage from decommissioned (unlined) slimes dams
- Run-off from sidewalls of slimes dams (dissolving uranium crusts on the surface of the walls)
- Seepage from (unlined) return-water dams, toe dams
- Seepage from pollution-retention dams
- Seepage from sand dams
- Seepage from evaporation dams/pans
- Seepage from slimes dams irrigated with process water
- Run-off from contaminated areas not captured by stormwater-drainage systems
- Leakages from process-water canals, pipelines and dams (frequent pipeline burst due to increased ground instability)
- Spillages of process water (pipeline bursts, uranium-plant accidents …)
- Spillages/ run-off/ seepage from handling uranium concentrate (storing, transporting, etc.).

3.2.2 Gold mining-related 'off-site sources' of uranium

As a direct or indirect consequence of mining operations uranium-bearing material is transported ─ controlled or uncontrolled ─ from mine lease areas into the adjacent environment. Examples for the controlled export of uranium-bearing material include:

- Tailings used to fill nearby sinkholes, including sinkholes on mine property which are part of cavity systems that extend underground beyond the borders of the mine lease area. A particularly dramatic case of introducing contaminated material into a sinkhole ─ although this did not happen in a controlled manner ─ occurred when a sorter and crusher plant of

West Driefontein GM, treating uraniferous ore, was swallowed by a sinkhole along with 27 workers.

- Slimes discarded as suspended solids along with discharged process water subsequently settling in irrigation channels, settling ponds, dams and wetlands.
- Tailings or scrap metal used as building material outside the mine property.

Examples of uncontrolled release of uranium-contaminated material from mine properties into the environment include:

- Tailings particles from slimes dams eroded by water (including dam breaches)
- Slimes spillages due to pipeline bursts, etc.
- Windblown dust from tailings depositing on sealed surfaces (towns) and open water surfaces (dams)
- Gold-bearing slimes illegally used to extract gold outside mine properties. Apart from the associated transport of uranium contained in such slimes, illegal extraction of gold may also lead to contamination of affected areas with mercury (Hg), frequently used as leaching agent for gold (through amalgamation).

As a result of the continuous release of uranium-contaminated mine effluents, uranium is frequently found to accumulate in sediments of receiving water bodies outside mine properties. Such ‘off-site reconcentrations’ of uranium mainly occur because of physicochemical processes (such as precipitation, coprecipitation and adsorption), as well as biological processes incorporating uranium into biological tissue (‘bioaccumulation’). Under certain conditions such off-site accumulations of uranium may turn into (then secondary) sources of water contamination. Uranium enrichments in the environment are frequently observed in:

- Sediments of fluvial systems, including:
    - Fine-grained (clay/silt) and often organic-rich sediments (sludge) of dams
    - Coarse sediments (sand/gravel) of stream channels
    - Wetland sludge/subaquatic soils (dy, gyttja)
    - Floodplain sediments and soils
- Salt crusts (hard pans) forming owing to evaporation of contaminated water on:
    - Topsoil of floodplains
    - Sediments of riverbanks
    - Vegetation (dead wood, cut plants)
- Organic matter of aquatic ecosystems such as:
    - Algae, phytoplankton

  - Aquatic plants (wetland reeds, floating plants …)
  - Subaquatic biofilms (on sediments, etc.)
  - Aquatic fauna (benthos, crabs, frogs, fish …)

3.2.3 Non- gold mining-related sources of uranium

Besides the afore-mentioned sources of uranium contamination, a few further (potential) sources exist in the Mooi River catchment which are not directly linked to gold-mining activities.

With the Nuclear Fuels Corporation of South Africa (NUFCOR) as one of the world's largest continuous producers of uranium oxide (GCIS, 2003) located in the upper part of the Wonderfonteinspruit catchment (near the town of Westonaria), one of the potential sources of uranium contamination is indirectly linked to gold mining. At NUFCOR uranium concentrates supplied by four uranium-producing gold mines (*inter alia* by Western Areas GM) iare refined to nuclear fuel for the nuclear power plant in Koeberg (near Cape Town). This involves the treatment of yellow cake[8] (Triuranium octaoxide: U_3O_8) including roasting and adding of metal oxides, as well as transporting of uranium concentrate (raw material and final product) by trucks (pers. commun. Wade, P., 2003).

A truly non-gold mining-related potential source of uranium is a fertiliser production facility in Potchefstroom (Kynoch Fertilizer) using phosphates, which are known to contain elevated levels of uranium (ATSDR, 1999). Run-off from the plant and adjacent areas, which are visibly covered with white dust from production processes, as well as seepage from an adjacent slimes dams with waste products (several tens of metres above ground) may lead to elevated uranium levels in receiving surface and groundwater. This even more so since a number of small non-perennial streamlets run in close vicinity to the factory and its tailings dam. One of the receiving streams is the Wasgoedspruit that discharges into the Mooi River within Potchefstroom.

In case of elevated uranium concentrations in water drawn from Boskop Dam as the main reservoir of the water-supply system of Potchefstroom and receiving water from the Wonderfonteinspruit, it is likely that sludge of the water-purification and sewage plants contains elevated uranium levels. Where such sludge is used for agricultural purposes (e.g. application on cultivated soils), a possibly associated soil contamination with uranium should be investigated prior to further utilisation.

Since both facilities may contribute to elevated uranium levels in the receiving Mooi River that would otherwise be entirely attributed to the Wonderfonteinspruit, these potential sources are mentioned even though they fall outside the Wonderfonteinspruit catchment.

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[8] Which is in fact olive green rather than yellow as the name would suggest, ATSDR, 1999

3.3 Pathways and mechanisms of uranium migration from mining sources into the environment

Water is the main agent for transporting uranium from potential sources into the environment, either in dissolved, colloidal or in particulate form. For the purpose of this study, no distinction between dissolved and colloidal is made. All uranium in water samples passing through 0,45 µm filters is regarded as dissolved.

In addition to the aqueous pathway uranium can also be transported via the atmosphere, e.g. as windblown dust from slimes dams and in gases like radon as a product of the radioactive decay of uranium. Because of the extremely long half-life of the major isotope of natural uranium U238 (4,7 billion a) compared with the temporal scope of this study, changes in the uranium concentration due to its radioactive decay and the migration of daughter products can be neglected. The main focus in this study is on major pathways that affect the quality of water resources in the Wonderfonteinspruit catchment. These include:

- Dissolution of uranium from solid phases in mined reefs, milled ore and tailings
- The waterborne transport of dissolved uranium from on-site sources into adjacent streams
- Transport of dissolved uranium within the fluvial systems, including immobilisation and remobilisation

3.3.1 Dissolution of uranium from solid phases

Leaching of uranium from underground ore

Uranium in mined gold reefs of the Far West Rand occurs mainly in its tetravalent form as uraninite or pitchblende (UO_2/U_3O_8). Having been formed under reducing (anoxic) conditions, such tetravalent minerals are unstable in the presence of free oxygen and tend to release uranium into surrounding waters. Since mining allows for excessive contact between the uraniferous rock face and oxygen, the rate of uranium release from mined reefs is likely to be significantly higher than from natural (undisturbed) ore bodies as they are found e.g. in the Northern Cape (Namaqua region). Groundwater of that region, displaying up to 2 mg/l uranium, suggests that even higher maximum concentrations are to be expected in fissure water of gold mines in the Far West Rand. This is supported by the fact that applications for nuclear licenses from gold mines in the study area were declined by the NNR, since levels of radioactivity in effluents leaving the property of such mines exceeded applicable limits set by the NNR (Khoathane, 2003). Although uranium does not form sulphides, which might be transformed into much more soluble sulfates as is the case with many other heavy metals, sulphide oxidation (= acid mine drainage) was frequently observed to accelerate the dissolution of uranium from solids and to increase uranium concentration in mine effluents by several orders of magnitude (Mrost and Loyd, 1970). Apart from uranium grades of the ore and the extent of oxidisation, the uranium concentration in surrounding fissure water is also determined by the contact time between ore and water and the flow rate. Carbonate-rich groundwater, such as dolomitic fissure water, frequently forms calcite scales in underground pipes and canals containing several thousands of mg/kg uranium. In addition to this secondary (hexavalent) uranium mineralisation is frequently observed in fissure-water environments underground (Wendel, 1998).

Leaching of uranium from processed ore

To enhance the leaching of uranium from the mined ore the latter is crushed and milled to a particles size of 70–100 µm, increasing the reactive surface area of the ore considerably. Exposed to concentrated sulphuric acid as the most commonly used leaching agent in SA, about 90 per cent of the uranium could be leached from the ore. Assuming a water:solid ratio of 1:1 (50% water) the leachate (pregnant solution) may have contained between 90 and >300 mg/l uranium depending on the uranium grade of the leached ore. With uranium concentrations of up to 58,000 mg/kg in kerogen seams of the Carbon Leader Reef, peak concentrations may have been up to 200 times higher (Cole, 1998).

Leaching of uranium from tailings

While in tailings of uranium plants only 10 per cent of the original uranium concentration of the ore is left, tailings of gold plants which are not, or are no longer, leached for uranium contain 100 per cent of the original uranium concentration which ranges from >50 mg/kg to >300 mg/kg on average. Displaying an enlarged reactive surface after milling, tailings are susceptible to the oxidation of remaining sulphides (mainly pyrite) and the associated leaching of uranium (acid mine drainage). This natural process is aided by bacteria and was under consideration to be used in industrial leaching of uranium from milled ore in the early 1970s (Mrost, 1970). In pilot studies it was found that the activity of bacteria is mainly determined by temperature and, more importantly, the availability of free (atmospheric) oxygen. In deeper layers of slimes dams the latter is often the limited factor, since airflow between tailings pores and the atmosphere is increasingly impeded the further away the slimes are from the surface of the dam (interface to the atmosphere). The main driving force for the airflow is the day-night difference of air temperature that leads to changing air volumes, with associated ‘pumping’ or ‘sucking’ effects. Under the climatic conditions of the South African Highveld, where most of the slimes dams are located and comparable long sunshine hours with high temperatures during the day and rather cold nights prevail, this mechanism allows for sufficient airflow up to a depth of about 2–3 m below surface. Below this depth bacteria-aided AMD and associated leaching of uranium from slimes particles slow down significantly, often also indicated by a change of the colour of slimes. Apart from progressively decreasing temperature fluctuations in deeper layers of the slimes dams, the formation of piezometric surfaces by porewater may also contribute to limit the depth of pyrite oxidation in slimes dams.

Under conditions of sufficient aeration in shallow pans porewater of oxidised tailings displayed concentrations of dissolved uranium of up to ***150 mg/l***. That means, that off-site depositions of tailings eroded from slimes dams are particularly prone to AMD and the associated accelerated uranium releases. Since AMD was found to be temporarily impeded in water-saturated tailings (as occurring e.g. after rainstorms) (Mrost and Loyd, 1970), the release of contaminants from tailings washed into nearby streams (as is frequently observed) might be limited as long as such tailings remain covered by water (subaquatic). During dry seasons, however, when many non-perennial streams dry up, such sediments are likely to become rapidly oxidised, transforming uranium into more- soluble compounds. This is of particular concern shortly after the onset of rains when associated stream flow is likely to flush dissolved uranium downstream. Under the climatic conditions of the FWR this is particular likely to occur during early spring.

3.4 Transport of uranium along the aqueous pathway

3.4.1 Uranium from underground sources

Water from underground mine working that was in contact with uranium-bearing material such as mined and unmined reefs, secondary uranium minerals in water canals and pipes, dust from blasting operations and contaminated mining equipment is either pumped to the surface, evaporates (leaving dissolved solids and solid uranium behind) or lost as seepage to deeper and adjacent aquifers. Such waters include:

- Fissure water from overlying aquifers which might have been in contact with virgin ore,
- Fissure water from overlying mine workings that has been in contact with mined and therefore oxidised ore,
- Fissure water used to suppress dust of drilling and blasting operations (thereby turned into process water),
- Cooling water running through contaminated pipes with highly uraniferous scales,
- Water used for washing contaminated underground equipment,
- Water running through open underground canals of mine workings which contain secondary uranium minerals or uraniferous scales.

In cases where fissure water is treated to become potable water, traces of uranium might be removed by forced precipitation, leaving behind contaminated sludge in water-treatment plants. The discharge of such water via sewage works is not likely to constitute a major source of point contamination. However, sewage sludge of the purification (maturation) plants should be analysed for uranium.

Water used for dust suppression underground, dewatering of mine workings and cleaning underground mining equipment, however, is likely to contain higher concentrations of dissolved and particulate uranium (suspended solids). To remove the latter such water is frequently discharged via settlings ponds, where the majority of suspended solids settle, generating contaminated sludge. The discharge of such water might constitute a significant source of point contamination mainly with dissolved uanium. In many cases the water needs to be transported from the mining site to the receiving stream in open canals (furrows). Being exposed to evaporation (white) sulfate crust is frequently formed at canal walls. Such crusts are likely to be repeatedly redissolved when discharge volumes rise during night time, reflecting the higher pumping rates utilising cheaper off-peak tariffs for electricity. In such cases the onset of higher flow rates in canals after 22h00 hours might contain elevated uranium concentrations. Besides the redissolution of sulfate crust on canal walls, the increased volume of uraniferous water being discharged into the Wonderfonteinspruit is likely to increase the overall uranium load during night time in general. The same applies to weekends and holidays when higher pumping rates due to off-peak tariffs are used as well.

3.4.2 Uranium from processed ore

Water being in contact with processed uranium and gold ore includes:

- The leachate (pregnant solution) and flotation water from the metallurgical process (‘metallurgical process water’),
- Water used to transport tailings from the metallurgical plant to the slimes dams (slurry)
- Water decanting via the penstock from paddock areas of slimes dams and flowing to the return-water dam
- Return water being directed onto evaporation facilities
- Rainwater run-off from ore piles, metallurgical plants, etc.

Water used in the above processes usually displays high concentrations of uranium and other contaminants, and can therefore not be discharged into nearby streams. It is therefore reused in the metallurgical process as often as possible and only disposed of once it is no longer suitable for such purposes. A common way of disposing of such non-recyclable water is evaporating it in on-site ‘evaporation dams’ or ‘evaporation pans’. Owing to the nature of the water, sediments in evaporation facilities usually contain high concentrations of uranium, gold and other heavy metals which are frequently recovered in metallurgical plants. In many instances such evaporation facilities are not lined and seepage occurs. In examples from the Klerksdorp goldfield more than 90 per cent of the highly contaminated water did not evaporate but seeped into the (dolomitic) underground. Other losses occur as seepage from return-water dams of which the majority currently are also not lined, seepage from canals, leakages from pipelines, etc.

Another potential source of contamination is accidental spillage of process water within metallurgical plants or outside by bursting or leaking pipelines, etc. Such spillage usually drains into stormwater-drainage systems, which eventually discharge the highly contaminated water into the streams. Cases have also been reported in which stormwater- drainage systems were used to dispose of process water illegally.

To retain water from return-water dams which are overflowing owing to storm events, additional dams are often constructed ─ ‘buffer’, ‘pollution-retention’ or ‘pollution-prevention’ dams. Storm events exceeding rain intensities of 1:50a reoccurrence intervals are likely to cause spillages from such dams. Run-off from metallurgical plants, piles of freshly broken ore and other sealed surfaces on which contaminated material such as tailings dust is deposited may also contribute to the contamination of nearby streams once it is discharged via stormwater-drainage systems. Since rainfall in the Highveld mainly occurs during highly intensive thunderstorms, this pathway constitutes a significant source of potential (point) contamination of adjacent streams. This pathway is of particular concern during wet summer months (October–March).

3.4.3 Uraniu m from active and decommissioned slimes dams

Water potentially contaminated by tailings in slimes dams includes:

- Porewater in slimes dams and resulting seepage
- Seepage contained in toe dams of slimes dams
- Stormwater run-off (paddock, sidewalls, salt crust)
- Seepage and run-off from irrigation of vegetated sidewalls with process water

The term ‘porewater’ is used for all water contained in the space between tailings particles (pores) of slimes dams. In ***‘active’*** slimes dams (those onto which tailings are still being deposited) it is mainly fed by applied slurry water that seeps into underlying slimes, as well as by infiltrating rainwater. The area on which new tailings are deposited is called ‘paddock’ and defined by little slimes walls containing the water-tailings mixture (slurry). Surplus water from the paddock decants into a vertical drain through the slimes dam (‘penstock’) placed in the centre of the paddock to be stored in the return- water dam for renewed use in the metallurgical process. With slurry flowing toward the penstock, a puddle forms around it (‘pool area’) surrounded by a much larger area (95% of the total paddock area) of water-saturated tailings (‘beach area’). Evaporation rates from the pool area are almost equivalent to the potential evaporation from open water surfaces under Highveld conditions (as measured in Symon- or A-pans), and amounts to 4 mm/d. Compared with this, evaporation at the beach area (1 mm/d) only reaches 25 per cent, leaving more water to infiltrate into underlying tailings where it is largely protected from evaporation. This contributes to the formation of a phreatic surface (porewater table) several metres below the top of the slimes dam, which in turn drives seepage into underlying aquifers. In order to retain out-flowing seepage, ‘toe dams’ made of slimes material are installed at the foot of the slimes dam. The spontaneous formation of wetlands at the foot of slimes dams, which frequently can be observed, indicates a permanent elevation of groundwater levels in the vicinity of slimes dams due to the ongoing outflow of tailings-seepage throughout the year (Winde and de Villiers, 2002).

In many instances seepage migrates via groundwater in fluvial sediments of adjacent floodplain areas (‘alluvial aquifer’) into fluvial systems. Passing through highly sorptive floodplain sediments and peat bogs may remove some of the dissolved uranium from the contaminated groundwater, either by adsorption onto negatively charged surfaces of clay minerals and organic matter or coprecipitation along with insoluble compounds such as iron hydroxides. While this leads to lower uranium loads reaching the stream, it simultaneously contaminates floodplain soils and fluvial sediments. In low-lying areas of the microrelief of the floodplain, capillary ascending water from the shallow groundwater table frequently leaves extensive sulfate crusts on top of the floodplain soils once it has evaporated. Uranium concentration in such crusts was found to be up to ten times higher than in the tailings as actual source of contamination. The indication is also that neutral uranyl-sulfate complexes may form which largely prevent adsorption of uranium onto negatively charged surfaces of floodplain sediments (Payne, 1998; Winde, 2002). Being readily redissolved by rainwater, the sulfate crusts are likely to act as secondary source of stream pollution with uranium (Winde, 2002).

In addition, highly contaminated slurry water also infiltrating rainwater contributes to the formation of the phreatic surface. In ***decommissioned*** slimes dams infiltrating rainwater is the only source of porewater recharge that counterbalances the seepage losses. The equilibrium between recharge and seepage in decommissioned slimes dams under South African conditions is established at a level of about 25 m% water content in the tailings.

Because of its use in the metallurgical process slurry water already contains elevated concentrations of dissolved salts and uranium when it is discharged onto the slimes dams. In addition to this, uranium is leached from the large reactive surface area of the tailings particles that either contain 10 per cent of their original uranium concentration (if uranium has been leached) or 100 per cent in cases where uranium has not been recovered. AMD can significantly elevate the concentrations of dissolved uranium in seepage as illustrated by uranium concentrations of 30 mg/l found in seepage of a toe dam in the Klerksdorp area. AMD is of particular concern in old, decommissioned tailings in the upper part of the Wonderfonteinspruit catchment, where uncertain ownership and lack of maintenance also allow for significant water erosion of sidewalls to take place. Erosion does not only wash tailings particles into adjacent areas and promote AMD of such slimes spillages, but also increases AMD at the slimes dam itself by enlarging the reactive surface area through rills and gullies in sidewalls exposing more tailings to atmospheric oxygen.

Dissolution of uranium from slimes particles by percolating rainwater that is frequently of low pH (acid rain) and strong dissolution capacity, due to its low ionic strength, also contributes to the contamination of porewater and porewater-borne seepage. While high infiltration rates and zero topographic gradients largely prevent run-off of rainwater from the flat top of slimes dams, run-off from sidewalls can be significant. This is of particular concern not only because of the associated gully erosion but also owing to the re-dissolution of sulphate crust covering large parts of the tailings surface. Uranium being reconcentrated in such crusts of up to 10 times compared with underlying tailings material run-off from sidewalls can be highly contaminated. This is particularly true for the first flush of run-off reaching the stormwater-drainage system or the stream (overland flow).

While the outflow of seepage occurs throughout the year, run-off, under Highveld conditions, is confined to the wet summer months (October–March). Owing to the comparably small size of the catchment area, streams in headwater regions frequently show severe flow reduction or even fall dry during winter. However, because of the ongoing outflow of seepage from slimes dams which cover large proportions of some headwater regions in the study area, e.g. the Wonderfonteinspruit, the Tweelopiesspruit, the Loopspruit and the Klip River, a large amount of base flow during the dry winter months consists of highly contaminated seepage. Under such conditions uranium concentrations may rise significantly as samples from the Russell' Stream suggest, where ***>4 mg/kg*** dissolved uranium was found (IWQS, 1999). Since run-off from slimes dams might additionally contribute to stream contamination with uranium, the uranium loads of affected streams might be even higher in the summer months, despite possibly lower uranium concentration in the stream water.

3.5 Transport of dissolved uranium within the fluvial system

The distance and extent of downstream transport of dissolved uranium after it enters the fluvial system are determined by the net effect between immobilisation and re-mobilisation processes. **Immobilisation** comprises all processes which remove dissolved uranium from the water column by turning it into solid phases through different mechanisms such as:

- ***Adsorption*** (e.g. onto suspended solids, sediments, etc.),
- ***Flocculation*** (e.g. of colloids),
- ***Precipitation*** as uranium compound of low solubility,
- ***Coprecipitation*** along with hardly soluble compounds such as iron/manganese hydroxides/oxides,
- ***Biological incorporation*** into aquatic organic matter (biofilms, benthos, algae).

It needs to be stressed that the term 'immobilisation' is used in its chemical rather than a mechanical sense, since many of the resulting solid uranium phases are still mobile and can be transported further downstream as e.g. suspended solids. They are, however, unavailable for uptake by organisms, which take in solutions only.

Remobilisation, in turn, comprises all processes which liberate uranium from solid phases such as:

- ***Desorption*** (e.g. from contaminated sediments)
- ***Dissolution*** of solid phases (e.g. of secondary uranium minerals, uranium-bearing calcite, salt crusts, etc.)
- ***Biological decomposition*** of uranium-contaminated organic matter (e.g. detritus).

The term remobilisation in this context is also used in a chemical rather than mechanical sense and refers to all processes by which uranium is converted from solid phases into dissolved (solute) phases. It does not refer to the mechanical remobilisation (erosion) of contaminated sediments by increasing stream velocity, e.g. during flood events. However, such event-related mobilisation of contaminated sediments also needs to be considered when assessing associated risks, including events such as floods, droughts, veld fires, and accidental waste-water spillages that affect the hydrochemical environment, etc.

Almost all mechanisms of remobilszation and immobilisation are largely dependent on the pH and Eh of the aquatic environment in which they take place.

3.5.1 Immobilisation processes in the Wonderfonteinspruit

Decreasing uranium concentrations in water with increasing distance from the uranium input as found in the Wonderfonteinspruit (IWQS, 1999), as well as elevated uranium concentrations in sediments of the stream (Wade et al., 2002; Coetzee et al., 2002) indicate that uranium is immobilised during its fluvial transport. Uranium concentrations in sediments of 40–>600 mg/kg (**map 1**), which are far above local natural background levels (0,2–3 mg/kg), simultaneously indicate that immobilisation is the dominating process during the observed time period, turning fluvial sediments into sinks for uranium. If remobilisation had prevailed, no lasting uranium accumulations in stream sediments would have occurred.

It is, however, feared that the capacity of fluvial sediments to act as sinks for dissolved uranium from stream water may soon be exceeded, and all dissolved uranium would be transported downstream towards Boskop Dam ─ the main drinking-water reservoir of the Potchefstroom municipality (Coetzee et al., 2002). Another concern raised with regard to the sediments is the possible release of accumulated uranium from such sediments due to changing hydrochemical and hydraulic conditions in affected water bodies (Wade et al., 2002; Coetzee et al., 2002). Both concerns will be addressed in Chapters 7 and 10.

Important mechanisms for removing dissolved uranium from stream water are:

- Coprecipitation of uranium and other heavy metals along with ***precipitating iron-hydroxide gels*** and ***manganese oxide***
- Coprecipitation of uranium along with calcite due to ***biological decalcification***
- ***Adsorption*** of uranium onto sediments and suspended solids
- Formation of ***salt crusts*** by evaporation of contaminated water forming epsomite, gosslarite, gypsum (and jarosite) at the surface of water-saturated sediments
- Biological uranium uptake (***bioaccumulation***)
- Precipitation of ***tetravalent uranium*** in reducing environments
- Precipitation of uranium-bearing ***colloids.***

Coprecipitation of uranium along with Fe-/Mn- hydroxides/-oxides

Brownish amorphous flakes settling on the bottom of the stream visibly indicate the precipitation of iron hydroxides. Strong correlations between Fe and Mn, on the one hand, and uranium and other heavy metals, on the other, found in sediments of the KMS (Klerksdorp goldfield) suggest that uranium and other dissolved heavy metals are coprecipitated along with iron hydroxides and manganese oxides (Winde, 2002). The precipitation of iron hydroxides is particularly strong where subsurface seepage contacts atmospheric oxygen. Containing large amounts of dissolved iron such seepage puddles are often covered with thick crusts of FeOOH floating on the water surface. In streams the precipitation of iron hydroxides is triggered by well-oxygenated stream water that mixes with almost oxygen-free (reducing) seepage, keeping iron and manganese in solution. Apart from amorphous flakes, precipitating hydroxide also forms thin brown coatings on sediment particles such as quartz sand, which otherwise have no sorption capacity to retain uranium. Owing to increasing surface-mass ratios in smaller (spherical) particles, uranium concentration is higher in finer sediments affected by this process than it is in coarse ones. Simultaneously it means that there is no upper limit of sediments to accumulate uranium by this mechanism since new layers of uraniferous coatings can be added indefinitely. It was, however, found that in fast-flowing streams mechanical abrasion of such coatings during fluvial transportation reduces the thickness of coatings and releases parts of the coatings as suspended solids into the stream. Settling in low-flow areas such as dams and wetlands, such particles contribute to elevated uranium concentrations in sediments.

Apart from the presence of oxygen, precipitation of iron hydroxides is also determined by the pH-value. Without bacteria, precipitation of iron hydroxides only occurs if the pH is >7 and Mn-oxide forms only under even higher pH-values (8,5). In addition to this the rate of precipitation increases by a factor of 100 for each logarithmic unit of pH-increase.

Therefore, comparably high pH-values in well-buffered dolomitic water of the lower Wonderfonteinspruit aid the natural removal of uranium from the water column through Fe-Mn hydroxide/oxide precipitation. In the upper reaches of the Wonderfonteinspruit, however, where non-dolomitic rocks dominate the catchment and stream water shows significantly lower pH-values (4–5), it is to be expected that a higher portion of uranium stays in solution and is transported downstream (IWQS, 1999; Winde, 2003).

Coprecipitation of uranium due to biological decalcification

The term ***'biological decalcification'*** describes the precipitation of calcite ($CaCO_3$) due to the abstraction of dissolved carbon dioxide ($CO_{2\,(aq)}$) from water by green cells of aquatic plants as part of their photosynthetic activities. Using dissolved CO_2 for photosynthesis in order to produce biomass (with oxygen as by-product), aquatic organisms such as algae and phytoplankton disturb the calcium-carbonate–carbon-dioxide equilibrium, which determines the ratio between solid $_{(s)}$ and dissolved $_{(aq)}$ calcium carbonate ($CaCO_3$) in waters depending on the concentration of dissolved carbon dioxide according to the following equation.

$$CaCO_{3(s)} + CO_{2(aq)} + H_2O \rightleftarrows Ca^{2+} + 2HCO_{3\,(aq)}^{-}$$

While carbon dioxide-rich waters dissolve carbonate rock such as dolomite ($CaMgCO_3$) into free calcium ions (Ca^{2+}) and dissolved hydrogen carbonate (also known as *bi-carbonate, HCO_3^-*), which leads to chemical weathering known as 'karst', the extraction of carbon dioxide from such water triggers the reverse process, namely the precipitation of (solid) calcium carbonate (also termed '*calcite'*). Since this reduces the concentration of dissolved Ca in the water, this process is termed *'decalcification'*. If biological activity triggers the process it is termed 'biological' decalcification, whereas in cases where CO_2-losses into the atmosphere are responsible the term 'chemical decalcification' is used.

Hellman (1999) found for the River Rhine in Germany that biological precipitation of calcite, often forming crusts around suspended solids (*'Aufwuchs'*), simultaneously reduces the concentration of heavy metals in stream water. Results of a study conducted in the Klerksdorp goldfield indicate that calcite precipitation also removes dissolved uranium to a certain extent. Scales sampled at a canal in the Stilfontein mining area that discharges pumped dolomitic groundwater from deep underground mine workings of a defunct gold mine (1–1,3 km below surface) into the Koekemoerspruit show a high correlation between the concentration of calcium carbonate (those scales consists of up to about 74 wt% $CaCO_3$) and uranium and other heavy metals (Winde, 2002). In this particular case calcite precipitation was not only biologically triggered, but also caused by CO_2-exhalation from the water into the atmosphere due to lower atmospheric CO_2-pressure on the surface compared with the atmospheric pressure >1 000 m underground. The latter process supposedly is also of importance for the Wonderfonteinspruit catchment.

Chemical decalcification, due to reduced solubility of gas at higher water temperatures (Henry’s law), is also responsible for the scaling of water kettles in areas where dolomitic water is used. With most water kettles being used on a regular (daily) basis, such scales reflect the long-term quality of water boiled in the kettles. In order to place results from grab-sample analyses in perspective, those scales were analysed for their uranium concentration and will be discussed later in the report.

Because of the predominance of dolomitic rocks in the Wonderfonteinspruit catchment, calcite precipitation is likely to be an important mechanism for removing dissolved uranium from the water column. While in surface water of streams and dams biological decalcification dominates, in groundwater chemical decalcification induced by decreasing atmospheric CO_2 pressure, when pumped to the surface, might be more important. Once discharged into open canals, both processes might superimpose each other.

Along with changing concentration of dissolved carbon dioxide the pH of water also changes, rising as soon as sunlight for photosynthesis is available. After reaching a maximum in the late afternoon (around 16h00 hours), the pH gradually approaches its starting minimum, usually reached around midnight. Counterbalancing CO_2-losses by precipitating solid calcite, simultaneously CO_2 is released back into the water. The ability of water to compensate for CO_2-losses (‘buffer capacity’) is particularly high in catchments with carbonate rocks (e.g. dolomite). There photosynthesis-triggered fluctuations of the pH are normally significantly lower (about half a pH-unit/d) than in non-dolomitic water, where they can be as high as 2 logarithmic units per day (Winde, 2003).

In view of the significance of the pH for many immobilisation processes in natural waters, such fluctuations are an important factor influencing the uranium mobility in surface waters over time. In order to understand the hydrochemical dynamics of the Wonderfonteinspruit, real-time measurements were carried out. The results of those measurements are discussed later in the report.

Precipitation, in general, is to be regarded as a major mechanism for immobilising uranium in the Wonderfonteinspruit. Since it simultaneously produces new solid phases, which subsequently become sediment, no upper sorption capacity exists that would limit the ability of such sediments to bind uranium.

Adsorption of uranium onto sediments and suspended solids

Positively charged uranium and its compounds can be removed from the water phase by being adsorbed onto negatively charged surfaces of solid phases such as sediments and suspended solids. The ability of solid phases to bind uranium is called 'sorption capacity' and largely depends on the number of free valences and the size of the reactive surface area. Solids of particularly high sorption capacity found in the Wonderfonteinspruit include:

- Freshly precipitated iron-hydroxide gels, with a reactive surface area of up to 800 m^2/g,

- Detrital organic matter present, e.g. in wetland sludge, upper horizons of floodplain soils and dam sediments, mostly originating from decomposed plants, algae and other aquatic organisms (detritus),

- Flakes of coagulated organic substances mainly originating in sewage effluents (five sewage works, raw sewage from informal settlements, + manure discharge?)

- Clay minerals such as montmorillonite (three-layered), smectite, kaolinite (two-layered), mainly found in floodplain sediments, wetland and dams.

The adsorption of uranium onto freshly precipitated gel is only possible under neutral to alkaline conditions when the surface of such gels is negatively charged. Lower pH-values prevent adsorption owing to binding competition by increased concentrations of hydrogen ions.

Adsorption of dissolved uranium from groundwater or seepage onto fine-grained floodplain deposits and wetland sediments (sludge) often increases with contact time. Comparatively low flow velocities of water through such porous media favour adsorption. In floodplain areas next to slimes dams groundwater levels are frequently elevated by seepage to such an extent that lower-lying parts of the floodplain are submerged. These areas display higher uranium concentrations than less-frequently submerged parts of the floodplain (Winde, 2001). However, the encapsulation of uranium in organic complexes, such as humid acids, or neutral inorganic complexes, such as uranyl sulphates, may prevent the adsorption of uranium. Adsorption onto flakes of organic matter or coagulating organic substances are of particular importance downstream of sewage-work discharges. The sedimentation of such flakes and agglomerates in low-flow areas such as wetlands and dams may increase the uranium concentration of sediments in such areas significantly.

Formation of uraniferous salt crusts

Because of the evaporation of contaminated water from the surface of sediments, uranium and other dissolved solids remain as (usually white) crusts of secondary uraniferous minerals on the sediment surface. Crusts are preferably efflorescent in sediments where water ascends to the surface owing to capillary forces, as e.g. in lower- lying parts of floodplain areas with elevated groundwater levels and in bank sediments of stream channels (capillary fringe). Extensive crust covers were also observed on the surface of slimes dams and on cut ends of vegetation (grass and reeds), as well as on dead wood. Extensive crust formation was also found in wetland vegetation after being subjected to veld fires (Winde, 2002). As was frequently observed in the Wonderfonteinspruit catchment sandy 'beaches' of dams are also prone to the formation of salt crust where infiltrating dam water or ascending groundwater flows to the surface through capillary pores. Large salt crusts were also found on vertical walls of cut-off floodplain sediments adjacent to slimes dams.

Biological uranium uptake (bioaccumulation)

Of particular importance for uranium concentrations in surface water and sediments is the biological incorporation of uranium into aquatic organisms such as algae and phytoplancton. Owing to biological accumulation, algae tissue in a uranium-mining area in the Czech Republic contained up to 500 mg/kg uranium (dry substance, DS). Deposition of such algae after their death, therefore, can significantly contribute to high uranium concentration in affected sediments. Far less uranium was found in water lillies in a uranium-mining area of tropical North Australia,and crabs and fish sampled at the East Rand goldfield (Schoonbee et al., 1995). Another factor in biological uranium accumulation is biofilms on subaquatic sediments, although their uranium uptake has not yet been quantified. In addition to iron-hydroxide coatings, contaminated biofilms may explain why chemically almost inert sediment particles such as quartzitic sand or gravel were found to contain significantly elevated uranium concentrations (Winde, 2001).

In wetlands and floodplain areas the uptake of uranium by vegetation such as reed is to be considered. Schoonbee et al. (1995) found up to 100 mg/kg uranium (DS) in reeds. Burning such vegetation in annual veld fires and thereby concentrating the accumulated uranium in the ash, may also contribute to the contamination of floodplain sediments.

Precipitation of tetravalent uranium

Since the solubility of tetravalent uranium (U^{4+}) is significantly lower than that of its oxidised form (hexavalent U, U^{6+}), strongly reducing environments such as polluted groundwater, anoxic zones in wetlands and dam sediments may lead to the reduction of U^{6+} and its subsequent precipitation as U^{4+}. In geological history such processes (termed 'roll-front deposits' Lit.) generated many uranium placer deposits mined today (e.g. Wismut area near Seelingenstädt, parts of the Witwatersrand ore and others). In the catchment of the Wonderfonteinspruit such conditions may occur in shallow farm dams with highly eutrophied water owing to seepage from surrounding agricultural areas containing traces of fertiliser, the inflow of manure and sewage effluents, as well as to other sources of nutrients. Strongly reducing conditions may also be found in wetland areas where the typically high input of organic detritus naturally exceeds the rate of mineralisation. In areas where seepage from adjacent slimes dams seeps through such sediments they may act as geochemical barriers and remove dissolved uranium and other heavy metals.

Precipitation of uranium-bearing colloids

In mining water of the Wismut area (Germany) it was found that colloids might carry up to 25 per cent of all ‘dissolved’ uranium, depending on the pH. Colloids are the results of flocculation or precipitation processes without agglomerating to particles of visible size. Colloid-forming agents include Al- und Fe-hydroxides, as well as organic compounds (Zänker, 2002). Studies on how important colloidal transport of uranium in the Wonderfonteinspruit might be are not available yet. Changing hydrochemical environments, particularly pH and Eh conditions and the ionic composition of water, may lead to flocculation and subsequent precipitation of colloids.

3.5.2 Possible mechanisms of remobilisation of uranium in the Wonderfonteinspruit

Dissolution of secondary solid uranium phases

Of particular importance in this regard is the dissolution of ***uranium-bearing sulfate crust*** from surfaces of sediments of the riparian zone (bank sediments, floodplain soils) and tailings dams, since salt crusts are usually readily dissolvable. As mentioned earlier, this might be of particular concern where such crusts are redissolved on a regular basis owing to alternating water levels and in instances where a sharp contrast between wet and dry conditions (as is common in the South African summer) exists. In floodplains and wetlands this might frequently lead to efflorescence of extensive salt crusts during dry periods which then become redissolved during rain events, and subsequently rising stream-water levels, releasing pulses of dissolved uranium into affected streams.

The dissolution of other uraniferous precipitation products such as ***Fe/Mn-oxides/hydroxides*** and ***calcite*** is less quick and likely to require longer periods of changed hydrochemical conditions. Conditions favouing the dissolution of calcite are, e.g., high CO_2-concentrations and low pH-values in surrounding water for sufficiently long periods of time (months to years?). Redissolution in general is a slow process and not likely to produce sudden changes of uranium concentrations in streams.

Desorption

Desorption of uranium may occur if the pH of surrounding water drops (H^+-competition for free valences) or the EC rises (other ions competing for free valences on sorbants). It usually only affects a rather small proportion of uranium (the ‘weakly bound’ one as determined in sequential leaching procedures) (Wade et al., 2002). The possible remobilisation processes described here are investigated experimentally in the sequential extraction study as discussed later in the report.

Decomposition of organic matter containing uranium

With shallow farm dams frequently intercepting the course of the Wonderfonteinspruit and offering ideal conditions for the growth of algae, it is likely that uranium is accumulated in tissue of the latter (bioaccumulation). In the process of being deposited on top of the sediment after death, and becoming mineralised, uranium might be liberated or contributes to the uranium contamination of the affected sediment. This also applies to biofilms frequently found on fluvial and limnic sediments.

Since uranium also accumulates in wetland vegetations such as reeds (Schoonbee et al., 1995), the annual burning of wetlands may return the removed uranium to the soils in the form of contaminated ash. Over long-term periods this practice is likely to increase uranium concentration in topsoil of wetland sediments.

Fluvial erosion and sedimentation

Uranium-contaminated sediments can also be transported downstream during flood events after being hydraulically resuspended (eroded). Having once been brought into suspension, such sediments are also distributed as suspended solids across inundated floodplain areas. Samples of freshly deposited sediments (termed ‘flood deposits’) taken after a flood event in the upper Wonderfonteinspruit from rock surfaces (no possible mixing with underlying uncontaminated soil) displayed an average uranium concentration of 68 mg/kg (Winde and de Villiers, 2002). With an order of magnitude above the natural uranium concentration found in the affected floodplain soils, the deposition of the suspended stream sediments leads to the contamination of topsoil of rather large areas. The resulting patterns of contamination are determined not only by the concentration of uranium in the flood deposits, but also by the hydrodynamics of flooding and the horizontal distance of affected floodplain soils from river banks.

4 Identification of contaminants and contaminated sites (H. Coetzee and G. Ntsume)

A reconnaissance sampling exercise was undertaken in 2001, with the aim of identifying contaminated sites, as well as identifying the priority contaminants in the catchment. Samples were collected at sites throughout the catchment, as well as a background sediment sample from Klerkskraal Dam. Klerkskraal Dam was selected as a background site as it is situated in similar geology to the Wonderfonteinspruit, but has no direct waterborne impacts from gold/uranium mining. There is, however, a possibility of some windblown contamination from slimes dams in the catchment.

The sampling sites are listed in Table 2 and presented on Figure 5.

Table 2. Sampling sites for the reconnaissance samples

Sample	**Date collected**	**Description**	**Latitude**	**Longitude**
W1	23 May 2001	C2H060Q01 ─ Doornfontein canal	-26,370668	27,252314
W2	23 May 2001	C2H069Q01 ─ DWAF weir	-26,370014	27,249376
W3a	23 May 2001	Andries Coetzee's Dam	-26,369585	27,241580
W3crust	23 May 2001	Andries Coetzee's Dam	-26,369730	27,241581
W4	23 May 2001	Andries Coetzee's Dam	-26,370300	27,240450
W6	23 May 2001	Andries Coetzee's Dam	-26,373411	27,237310
W7	23 May 2001	Sediment in floodplain on Carletonville–Randfontein road	-26,310838	27,531313
W8	23 May 2001	R559 Road Bridge	-26,266585	27,700986
W101	15 Aug 2001	Andries Coetzee’s Dam	-26,372067	27,240550
W102	15 Aug 2001	Andries Coetzee’s Dam	-26,372067	27,240550
W103	15 Aug 2001	Muiskraal	-26,436383	27,151433
W105	15 Aug 2001	Klerkskraal Dam ─ Background	-26,225167	27,151667
W106	15 Aug 2001	Small dam downstream of Khutsong Water Care Works	-26,350039	27,313169
W107	15 Aug 2001	Below Carletonville	-26,314939	27,382778
W108	15 Aug 2001	Attenuation Dam	-26,213355	27,742100
W109	15 Aug 2001	Below Kagiso	-26,156356	27,765394

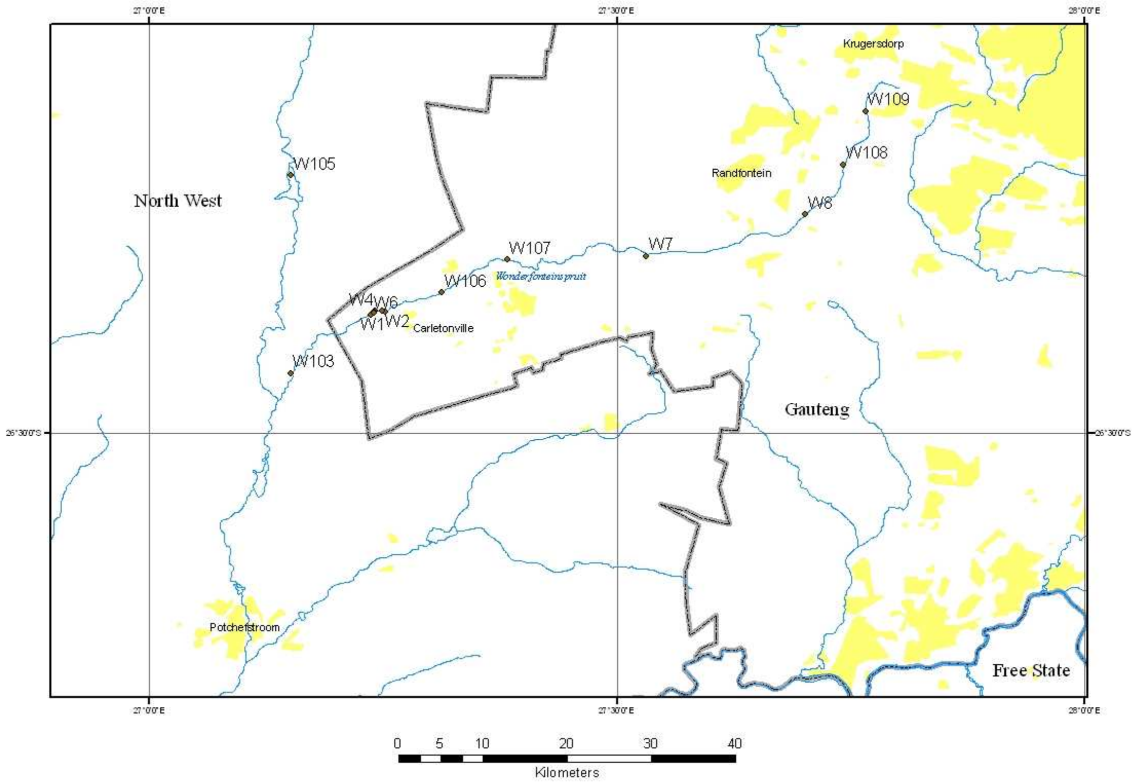

Figure 5. Locations of sampling points for the reconnaissance sampling campaign

In selecting these sites, the following criteria were used:

1. Sites were selected to be representative of the wetland areas in the catchment. Wade et al. (2002) describe the processes by which metals are concentrated in wetland sediments. Since one of the aims of the study is to compile an inventory of, and to quantify, the contaminated sediments in the catchment, likely sites were sampled.

2. Where possible, sites used in previous studies were chosen. This allows the results to be related to DWAF sampling programmes, as well as allowing an estimation of the concentration variations within specific sites.

3. Andries Coetzee's Dam was repeatedly sampled, as it has been identified as a critical hotspot within the catchment. It is also the first dam on which all mining activities within the catchment will have a potential impact. The repeated sampling of different parts of the sediment body within this dam allows the identification of different processes which concentrate metals.

4. Klerkskraal Dam was sampled as a background sampling point. Klerkskraal may receive some windblown dust from the mining activities within the catchment, but lies on geology (Malmani Group dolomite) similar to the largest portion of the Wonderfonteinspruit and has no gold/uranium mining located upstream of it.

4.1 Results

The results obtained are presented in Table 23 and 24 in the Appendix. In order to achieve the aims of this phase of sampling, the data have been used to compile a Tier-1 Risk Assessment (USEPA 1992) and to identify contaminants of concern.

4.1.1 Tier-1 risk assessment

The US EPA Tier-1 Risk Assessment, as described by Wade et al. (2002), has been applied to a subset of the data. In this assessment, a trigger level, typically a legislative or regulatory standard, is selected and measured concentrations compared with this standard. The risk quotient is defined as

$$\text{Risk Quotient} = \frac{\text{Measured Concentration}}{\text{Legislative/Regulatory Limit}}$$

Since South Africa does not have legislated limits for most contaminants in soil, values from the European Union (ANTEA, 2000) have been used. For radioactive elements, the South African National Nuclear Regulator’s (NNR) level for exclusion from regulatory control of 0,2Bq/g has been applied. It should be borne in mind that this level does not necessarily imply a public health threat, but that a conservative level has been deliberately chosen to ensure the protection of the public. This exclusion limit is, however, the correct level for a Tier-I assessment, as it allows the separation of those sites where uranium concentrations are so low as to be of “no regulatory concern” from those where additional study, in the form of higher-tier risk assessments, is necessary, and regulatory measures may be warranted. Unfortunately, no guideline level based on the chemical toxicity of uranium is available for South African soils. This level has been converted to mg/kg concentrations for the sake of consistency with the data presented in this report.

The data for a selected set of metals is presented in Table 25 in the appendix. In this table, concentrations with risk quotients between 0,5 and 2 are presented by shading in grey, while risk quotients greater than 2 are presented in black. This table allows the identification of sites where significant contamination has occurred. These data are summarised in Figure 6.

Based on this assessment and the radionuclide results reported by Wade et al. (2002), the entire study area, including the background site, is seen to be of environmental concern. It is therefore necessary that these values are placed in perspective.Figure 6. Box and whisker plot, showing the range (min.-1st quartile–median-3rd quartile max.) Tier-1 risk quotients for sediment analyses in the Wonderfonteinspruit. Risk quotients greater than 1 require follow-up studies and possibly remedial action.

Table 3 shows mean values for a range of rock types (Turekian and Wedepohl, 1961), compared with the same guideline levels as the Wonderfonteinspruit samples. It is interesting to note that a number of these standards are exceeded by naturally occurring rock types. The mean values for the Wonderfonteinspruit samples do, however, significantly exceed both natural concentrations and levels of regulatory concern for Co, Zn, As, Cd and U.

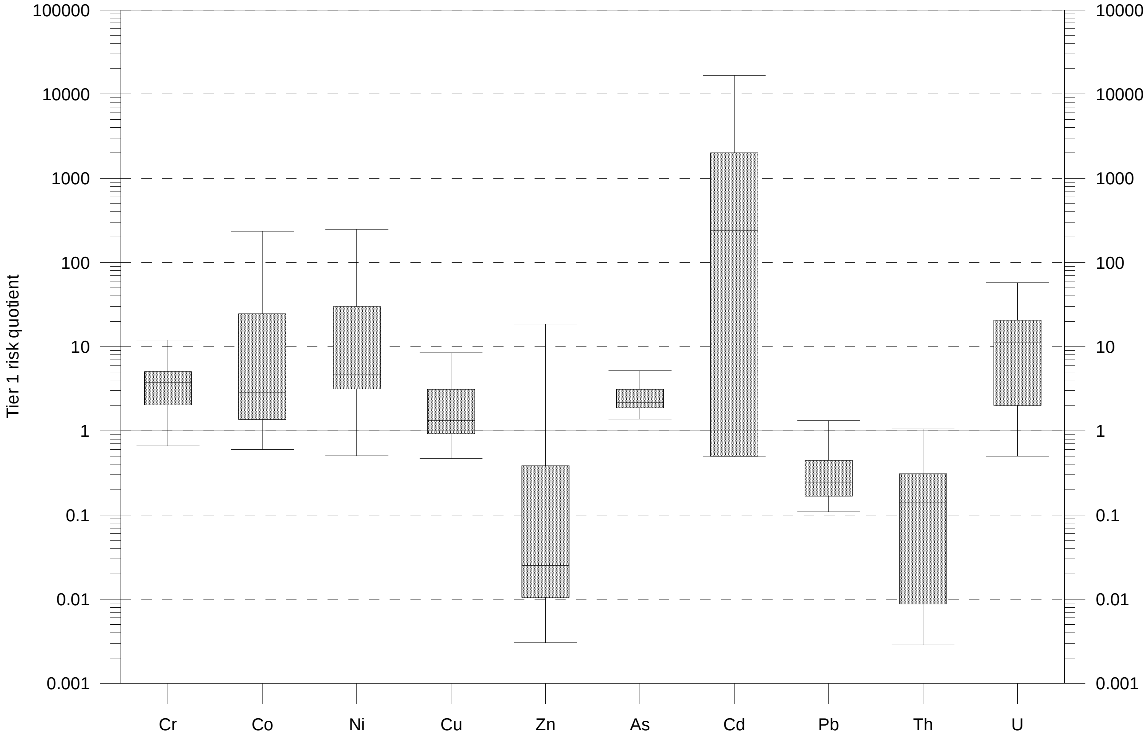

Figure 6. Box and whisker plot, showing the range (min.-1st quartile–median-3rd quartile max.) Tier-1 risk quotients for sediment analyses in the Wonderfonteinspruit. Risk quotients greater than 1 require follow-up studies and possibly remedial action.

Table 3. Concentrations of selected heavy metals in a range of rock types (Turekian and Wedepohl, 1961), compared with EU and NNR regulatory standards.

Element	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	**Th**	**U**
Std mg/kg	*65*	*20*	*35*	*36*	*4500*	*19*	*0.001*	*85*	*50*	*16*[9]
Source	*EU*	*EU*	*EU*	*EU*	*EU*	*EU*	*EU*	*EU*	*NNR*	*NNR*
Ultrabasic	**1600**	**150**	**2000**	10	50	1	**0.1**	1	0.004	0.001
Basaltic	**170**	**48**	**130**	**87**	105	2	**0.22**	6	4	1
Hi-Ca Granitic	22	7	15	30	60	1.9	**0.13**	15	8.5	3
Lo-Ca Granitic	4.1	1	4.5	10	39	1.5	**0.13**	19	17	3
Syenites	2	1	4	5	130	1.4	**0.13**	12	13	3
Shales	90	19	68	45	95	13	**0.3**	20	12	3.7

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[9] This level is currently being revised by draft regulations, which raise the limit for regulatory concern from 0,2Bq/g to 0,5Bq/g.

Element	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	**Th**	**U**
Sandstones	35	0.3	2	1	16	1	**0.01**	7	1.7	0.45
Carbonates	11	0.1	20	4	20	1	**0.035**	9	1.7	2.2
Deep-sea Carbonate	11	7	30	30	35	1	**0.01**	9	1	0.1
Deep-sea Clay	90	**74**	**225**	**250**	165	13	**0.42**	80	7	1.3
Mean Wonderfonteinspruit sediment	**251.45**	**557.82**	**1120.78**	**75.64**	6621.78	**48.08**	**1.88**	30.61	10.13	**221.39**

All the sites sampled within areas where mining activities are taking place also show significant contamination with these elements.

4.1.2 Quantitative analytical results determined using X-Ray Fluorescence

Following the court action regarding the draining of the dam on the farm Blaauwbank in January 2003, it was felt that quantitative results were needed to confirm pollution. A suite of samples was collected for analysis by X-Ray Fluorescence (XRF) and sequential extraction (See Section 5). The sampling positions for these samples are presented in

Table 4 and on

Figure 7. The XRF results for these samples are presented on Table 26 in the Appendix.

Table 4. Localities of samples collected for quantitative XRF and sequential extraction analysis of sediments.

Sample No.	**Locality**	Lat	Lon
GN029	Kagiso ext 8	-26,144139	27,762528
GN030	Luipaardsvlei Dam	-26,217361	27,737667
GN031	Greuning Dam	-26,244750	27,732556
GN032	Donaldson Bridge	-26,269000	27,697972
GN033	Bridge over the Carletonville Pretoria Road at Oberholzer	-26,319194	27,381167
GN038	Tudor Dam	-26,135306	27,794889
GN040	Gerhardminnerbron	-26,484750	27,135222
GN041	Boskop Dam	-26,546417	27,112778
GN042	Blaauwbank Dam	-26,389139	27,212028
GN043	A. Coetzee Dam	-26,376778	27,236194
GN044	Khutsong Bridge	-26,341167	27,327944
GN045	Donaldson Dam	-26,284306	27,682278

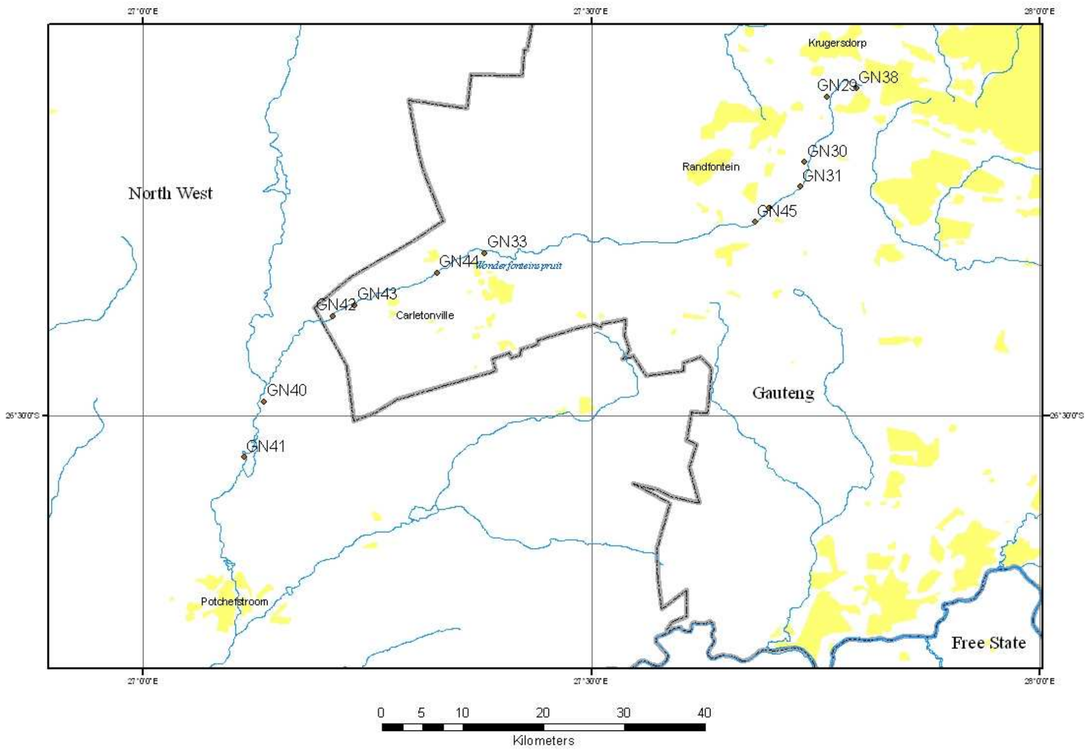


Figure 7. Sample localities for the XRF and sequential extraction studies

The site variability in these analyses is relatively large. A previous study (Coetzee et al., 2002) recorded a range of values for sediment samples collected in Andries Coetzee's Farm Dam. One sample was collected here in this study, with a measured uranium concentration of 77 mg/kg. In a previous study, 14 samples were collected with concentrations between 46 and 915 mg/kg. The mean value for these 15 analyses is 354±317 mg/kg (1-sigma). Unfortunately, sampling and analytical costs preclude repeatedly sampling each sampling site to quantify the in-site variation.

4.2 Compilation of semiquantitative and quantitative data

Semiquantitative data were used to identify the potentially contaminated sites, as well as the variables of interest, prior to the quantitative analysis of samples from these sites by XRF. This approach was used to limit the cost of analysis, XRF analyses typically costing approximately an order of magnitude more than ICPMS scans. During the course of this study and the DWAF-funded study on Andries Coetzee's Dam, a significant amount of both quantitative and semiquantitative data were collected from a single site. Unfortunately, both analytical methods show the large range of concentrations that can be expected from a single site, but plotting data from both analytical methods on a single histogram should allow visual comparison of the two methods. Such a histogram is presented in Figure 8. Figure 9 shows the four quartiles of data collected using the two methods. It is interesting to note that the data occupy a similar range, with the mean and median values of the XRF analyses slightly higher than those recorded using the semiquantitative ICPMS method.

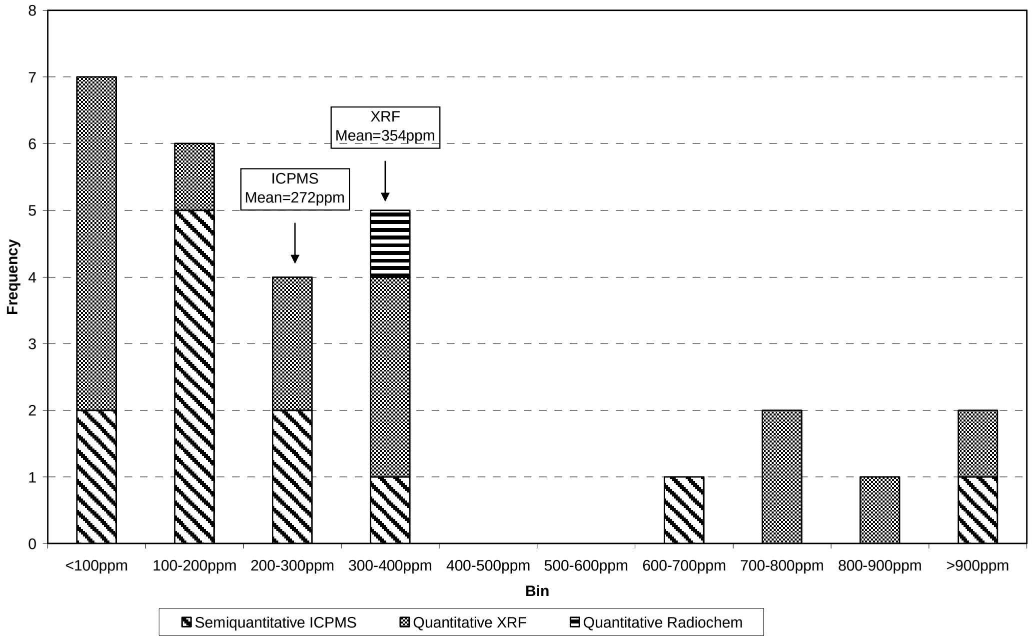


Figure 8. Histogram showing semiquantitative ICPMS, quantitative XRF and quantitative radiochemical data from Andries Coetzee's farm dam.

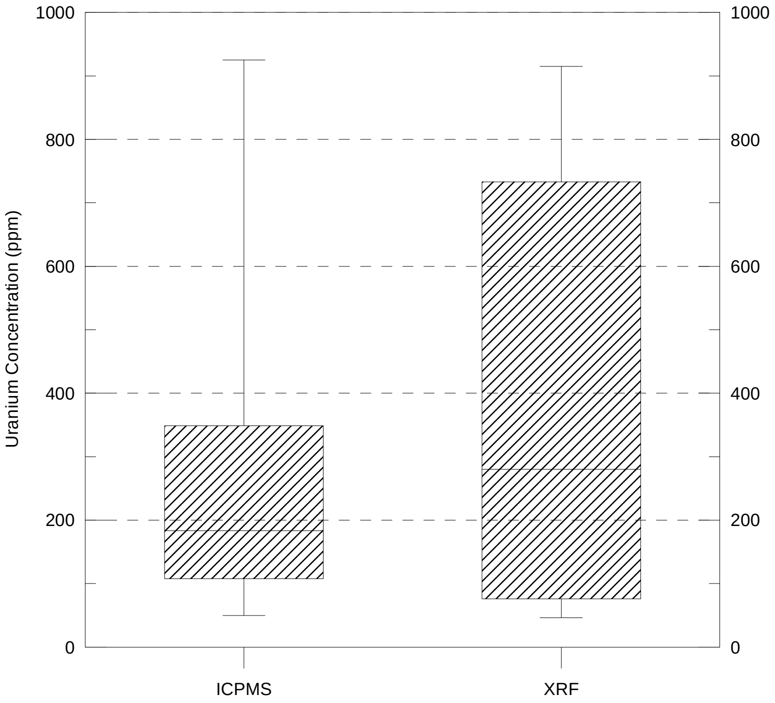


Figure 9. Box and whisker plot showing the extrema, 1st and 3rd quartiles and median of the semiquantitative – ICPMS (n=12) and quantitative – XRF (n=15) data determined on sediment samples from Andries Coetzee's Dam.

All available uranium-concentration data are summarised in Figure 10. The categories used to classify the uranium concentrations are reflected in Table 5.

Table 5. Categories used in mapping uranium concentrations

Category	Rationale
<background / ND	A local background value of 0,25 mg/kg has been recorded at Klerkskraal Dam. The detection limit for XRF analysis is 3 mg/kg. Values below this have been assigned ND values.
<16 mg/kg	16 mg/kg uranium is equivalent to an activity concentration of 0,2Bq/g, the limit for regulatory control set by the NNR.
categories>16 mg/kg	The data have been subdivided into a number of categories to identify the degree of contamination.

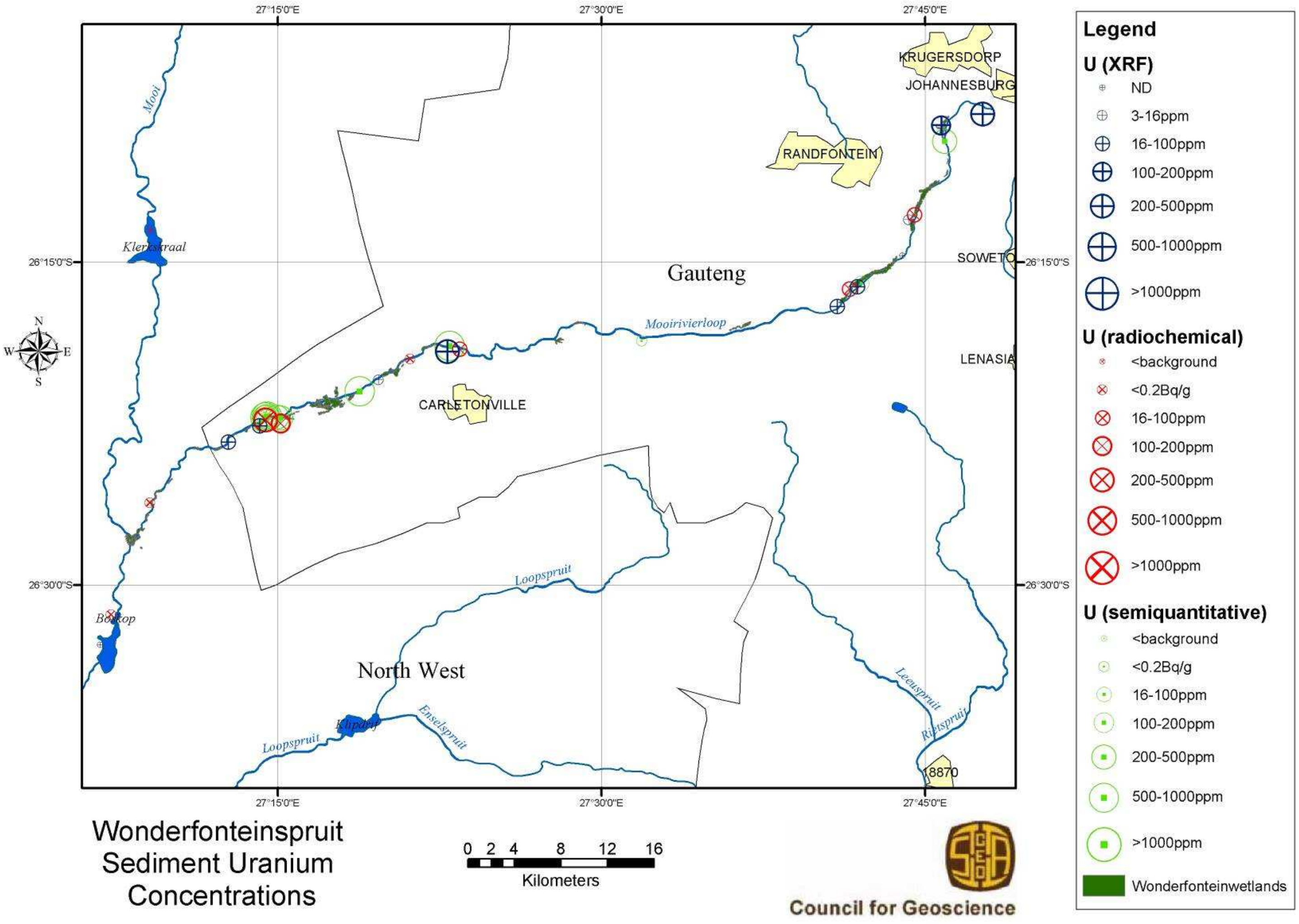


Figure 10. Uranium concentrations in sediments in the Wonderfonteinspruit catchment. Data have been divided into three groups, according to the method used for the analysis and grouped by concentration. The lowest-group boundary refers to the current limit for regulatory control

4.3 Identification of contaminants of concern

The second phase of the reconnaissance study involves the identification of contaminants of concern. Here the results of the ICP-MS scans have been compared with local background levels by normalising them to the concentrations recorded from Klerkskraal Dam. The normalisation process was facilitated by setting all values recorded at Klerkskraal that were below the detection limits of the method (~1 μg/kg) to one half of this level. In the case of uranium, the radiochemically determined value for Klerkskraal of 0,25 μg/kg (Wade et al., 2002) has been used. All normalised values below 1 per cent of the local background were set to 1 per cent, to limit the range of normalised values. These modifications were limited to very low concentrations only, and are not seen to significantly alter the outcome of the analysis.

The results for the full elemental scans are shown in Figure 11 to 11.

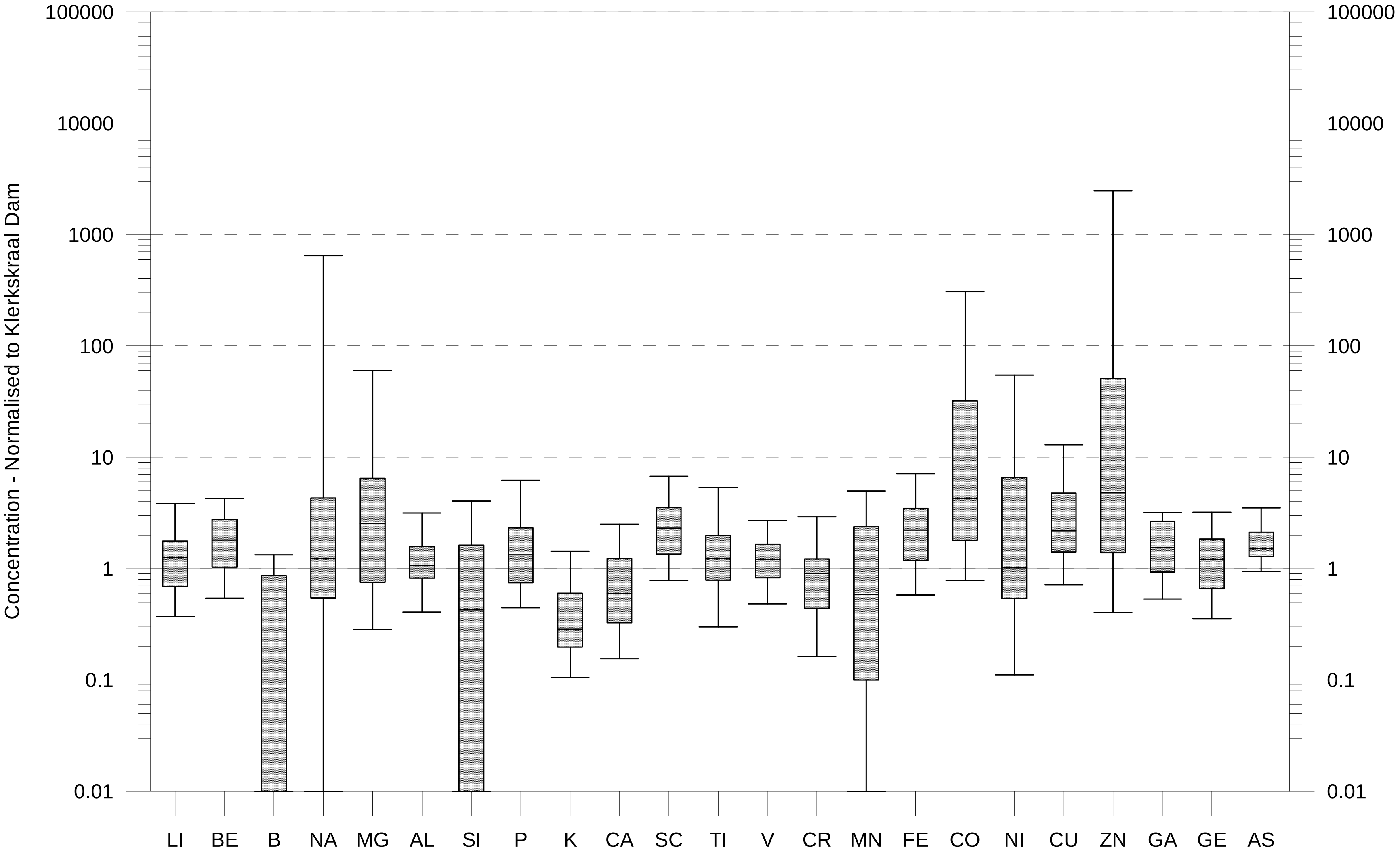


Figure 11. Box and whisker plot of reconnaissance sampling results of sediments for elements Li-As, normalised to Klerkskraal Dam

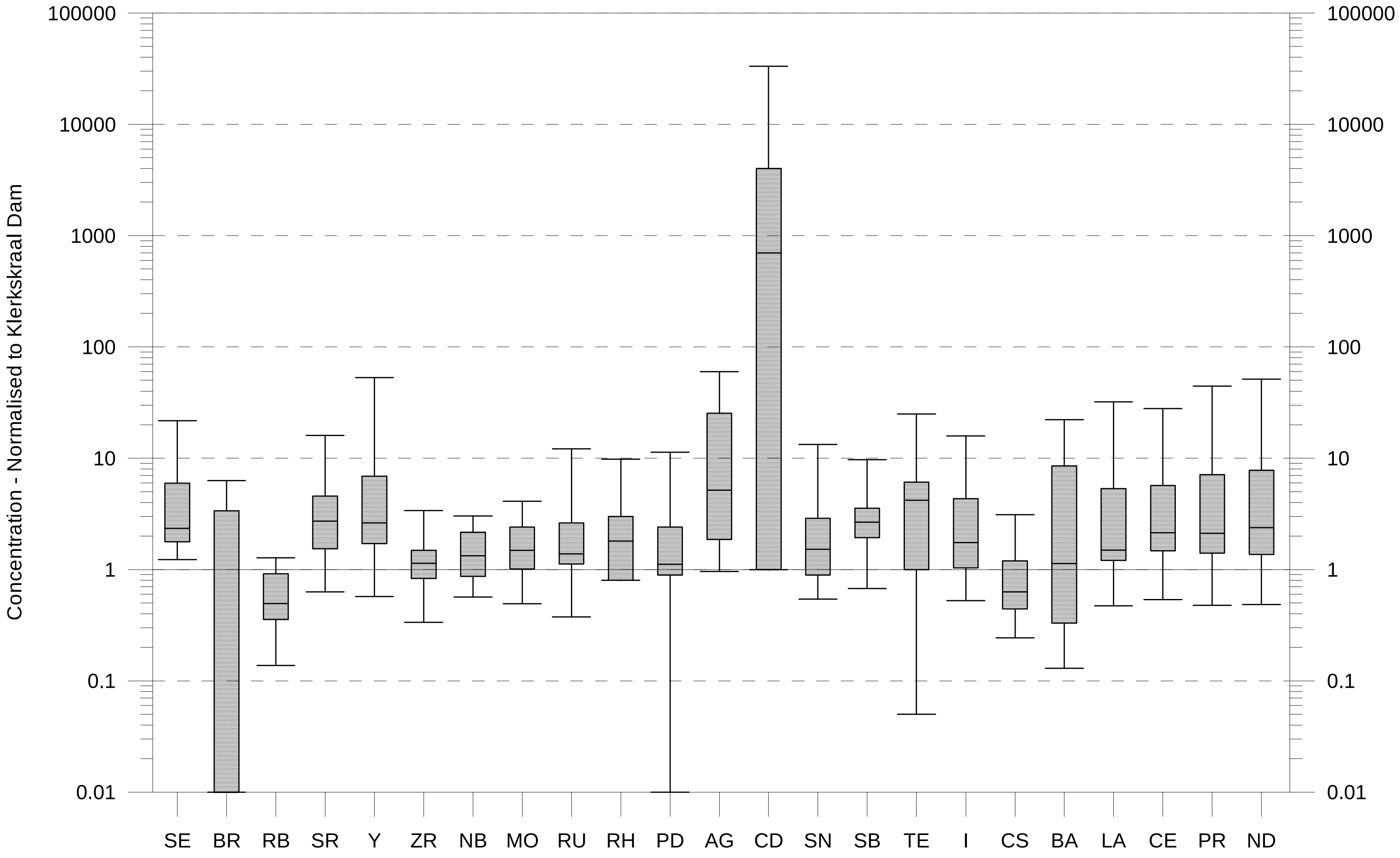


Figure 12. Box and whisker plot of reconnaissance sampling results of sediments for elements Se-Nd, normalised to Klerkskraal Dam

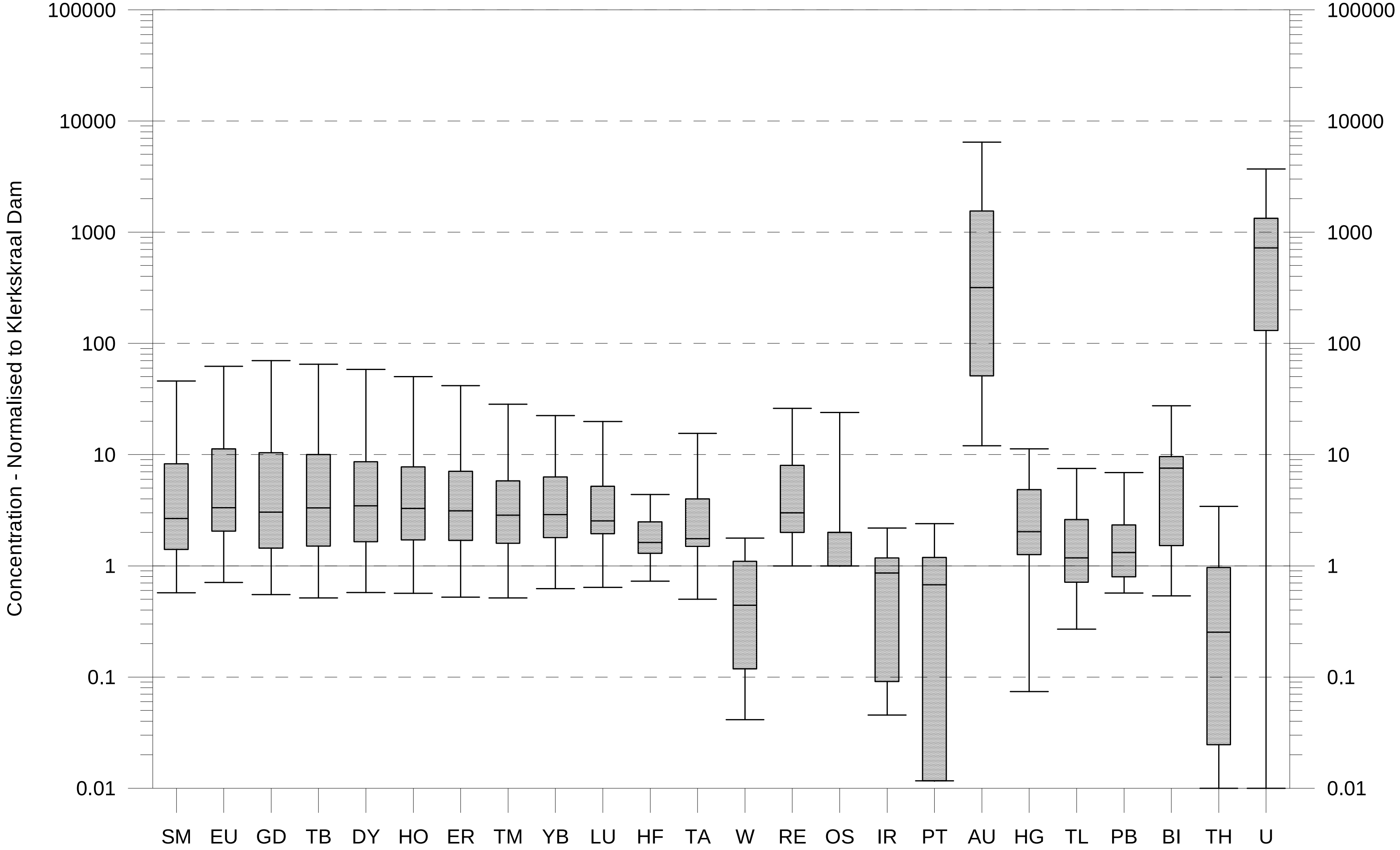


Figure 13. Box and whisker plot of reconnaissance sampling results of sediments for elements Sm-U, normalised to Klerkskraal Dam

On these figures, the extrema of the data are shown by the “whiskers”, while the box depicts the first and third quartiles of the data, with a horizontal line in the box at the median of the data values.

The values presented on these plots allow the identification of the contaminants of greatest concern. The contaminants of greatest concern are therefore uranium, cadmium, zinc and cobalt, with the median value for uranium concentrations measured in this sampling phase 720 times the local background and for cadmium, 700 times the local background.

Based on this analysis and the tier-1 risk assessment, Cr, Co, Ni, Cu, As, Cd and uranium require further action, with uranium and Cd potentially having the highest environmental impact.

The focus for this study will be on uranium, for the following reasons:

1. Uranium is emitted by a single industry, simplifying this study. The methodology developed for uranium should be applicable to other metals.

2. In recent years, uranium has been a major public and regulatory concern within the catchment. A detailed study, such as this, which aims at improving our understanding of uranium in the catchment, could significantly reduce public uncertainty.

3. It is felt that the resources available for this study allowed a relatively high degree of detail for a single element. For the reasons mentioned above, uranium has been selected as a target element.

4.4 Distribution of uranium in sediments in the catchment

Based on previous studies mentioned above and reconnaissance sampling, the spatial distribution of uranium in 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, to reduce the inflow of water into the dolomite and the mine workings below. These two zones can be further subdivided as follows:

1. Upper Wonderfonteinspruit

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

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 ─ sampled coarser stream sediments Uranium ~ 50–60 mg/kg. Approximately equal to flood deposits sampled after February 2000 rain event.

2. Lower Wonderfonteinspruit

a. 1st 30-km pipeline over dolomite. Sediments last in regular contact with stream water approximately 30 years ago. A uranium concentration of 12 mg/kg has been recorded for sediment sampled in 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 minewater, is discharged into the catchment. Sediment uranium concentrations reach ~500 mg/kg.

c. In downstream farm dams uranium concentrations are still significantly elevated; uranium concentrations 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 (H. Coetzee and M. Rademeyer)

5.1 Lead isotopes in mining environments

Lead isotopes offer a unique insight into sites contaminated with waste from uranium or thorium mines, or mines containing elevated uranium and thorium concentrations, as the stable lead-isotope ratios reflect the decay of these elements over time. Naturally occurring lead is composed of four stable isotopes, with nominal masses of 204, 206, 207 and 208. Each of these isotopes has a different origin, since heavy isotopes are not generally fractionated in chemical processes taking place in the environment. The origins and significance of these isotopes are summarised in Table 6.

Table 6. Lead isotopes in mining environments

Isotope	**Origin**	**Significance in environmental studies**
^{204}Pb	Common lead ─ formed in cosmogenic processes	The ^{204}Pb content of a mass of rock remains constant over time, allowing normalisation of lead-isotope ratios to an invariant isotope
^{206}Pb	Radiogenic lead, which originates from the decay of ^{238}U	The ^{206}Pb/^{204}Pb ratio gives a measure of the amount of ^{238}U that decayed in the parent material.
^{207}Pb	Radiogenic lead, which originates from the decay of ^{235}U	The ^{206}Pb/^{204}Pb ratio gives a measure of the amount of ^{235}U that decayed in the parent material.
^{208}Pb	Radiogenic lead, which originates from the decay of ^{232}Th	The ^{208}Pb/^{204}Pb ratio gives a measure of the amount of ^{232}Th that decayed in the parent material.

The measured ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios therefore reflect the U/Pb and Th/Pb ratios at the time of ore formation and the age of the ore. Witwatersrand gold ores have extremely high U/Pb ratios and, being old (~3 billion years), highly radiogenic ratios. These can be applied diagnostically to identify contamination from these ore deposits and have also been used to identify specific contamination streams (Eglington et al., 2001).

Lead concentrations in water are often extremely low, requiring special analytical techniques that were not available for this project. Furthermore, lead is adsorbed onto sediment phases, creating an integrated record of past contamination, avoiding temporary effects that would be created using grab water samples. Lead-isotope analyses were therefore undertaken on sediment samples to give a representative view of the mixing relationship between water in the catchment and local background conditions. It was also hoped that lead-isotope ratios may provide a diagnostic tool for the identification of individual contaminant streams.

5.2 *Analytical methods*

Pb-isotope analyses were carried out in the radiogenic isotope laboratory of the CGS using conventional anion exchange techniques and mass-spectrometric analysis. All ratios were normalised to accepted values for the NIST982 equal atom lead standard.

5.3 *Results*

$^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ data have been plotted, as these give an indication of both the uranium- and thorium-series concentrations in the source materials. Data from the entire catchment are shown in Figure 14. Note that the material from mines has an elevated $^{206}Pb/^{204}Pb$ ratio, representing the high U/Pb ratios in the ores (the uranium-238 has decayed to lead-206 over the time since ore formation). The variability of this parameter shows the variations in uranium content of the different ores that have been mined.

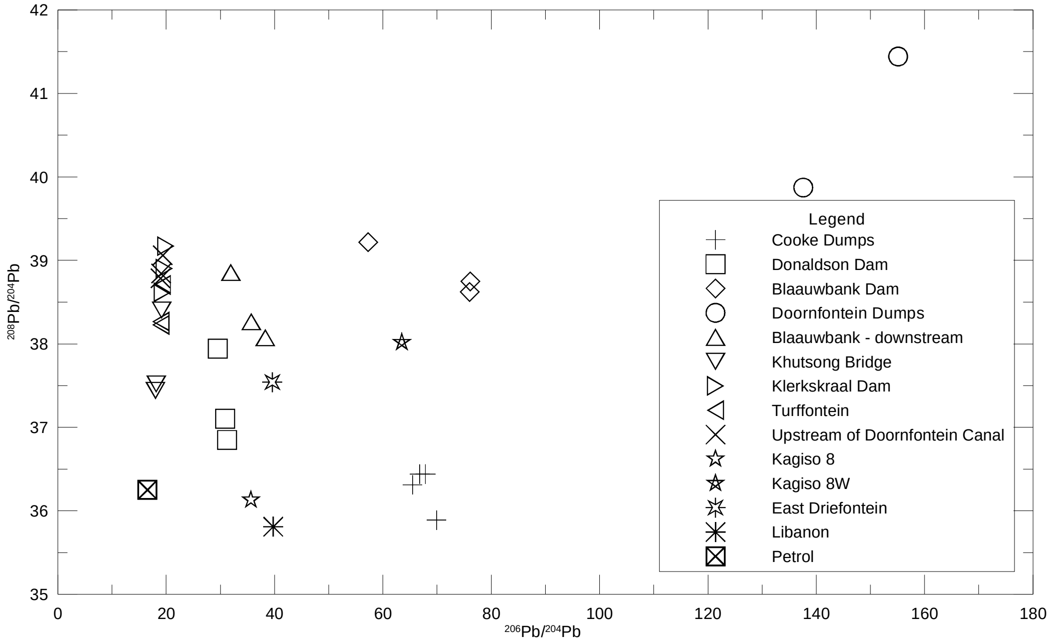


Figure 14. Uranogenic vs. thorogenic lead plot for data collected on mine wastes and sediments from the Wonderfonteinspruit catchment.

A number of clear trends are seen in these data:

1. Material from Doornfontein Mine is highly radiogenic, indicating the large concentration of uranium in the initial ore. This is diagnostic, and allows the direct identification of this or similar waste streams in the Blaauwbank Farm Dam, where, even after mixing with the lead from the natural environment, the ratios are still more radiogenic than any of the other mine waste. Clear pinpointing of the source would require the analysis of samples from all the mines in the vicinity.

2. The far-downstream and background samples have very similar $^{206}Pb/^{204}Pb$ ratios and only slightly varying $^{208}Pb/^{204}Pb$ ratios (Note that the x and y scales in Figure 14 vary

significantly). This probably represents local background ratios and the variability of these ratios.

3. The local background differs significantly from a mean value for South African leaded petrol, showing the contribution of natural environmental sources, as well as atmospheric fall-out due to the use of leaded petrol.

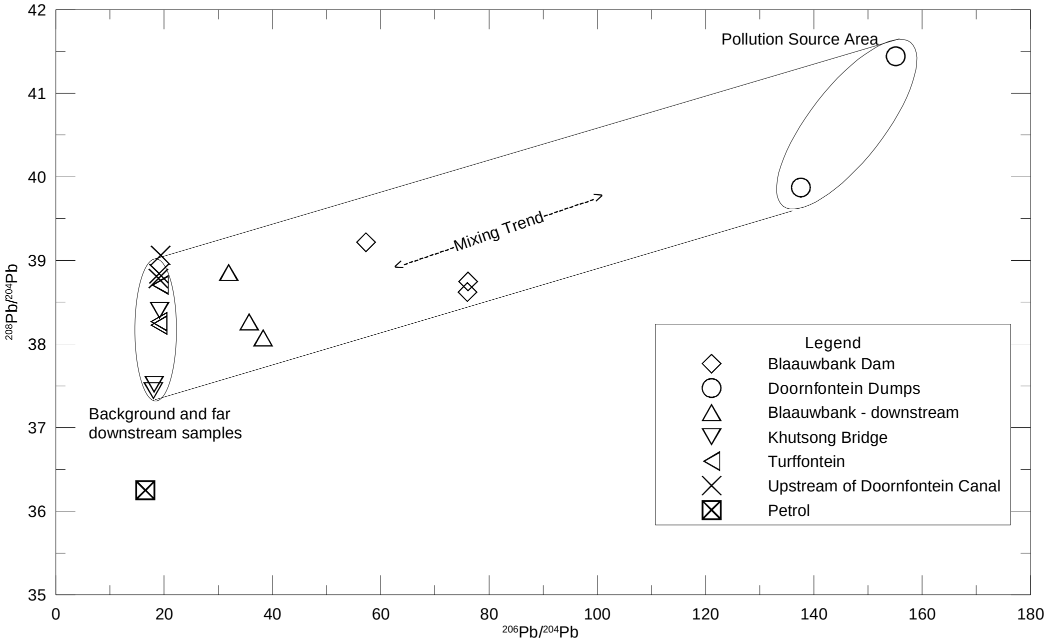


Figure 15. Uranogenic vs. thorogenic lead plot for data collected on mine wastes and sediments from the Doornfontein–Blaauwbank portion of the catchment.

Figure 15 shows a similar diagram from the vicinity of the Blaauwbank farm dam. Here a clear mixing trend between the pollution source and the sink in the sediments can be seen. A similar trend can also be determined between the Cooke Section, or isotopically similar wastes, and Donaldson Dam (see Figure 16). Again a more complete analytical dataset would allow better fingerprinting. Here the possible mixing relationships are not as well defined, either because of an incorrect choice of background, or because the background isotopic composition includes a component of mixing with pollution due to the use of leaded petrol. Other mining sources upstream may also play a role. Such mixing relationships have been defined for the Johannesburg and Pretoria areas, where leaded petrol plays a significant role in environmental contamination (Coetzee et al., 2002).

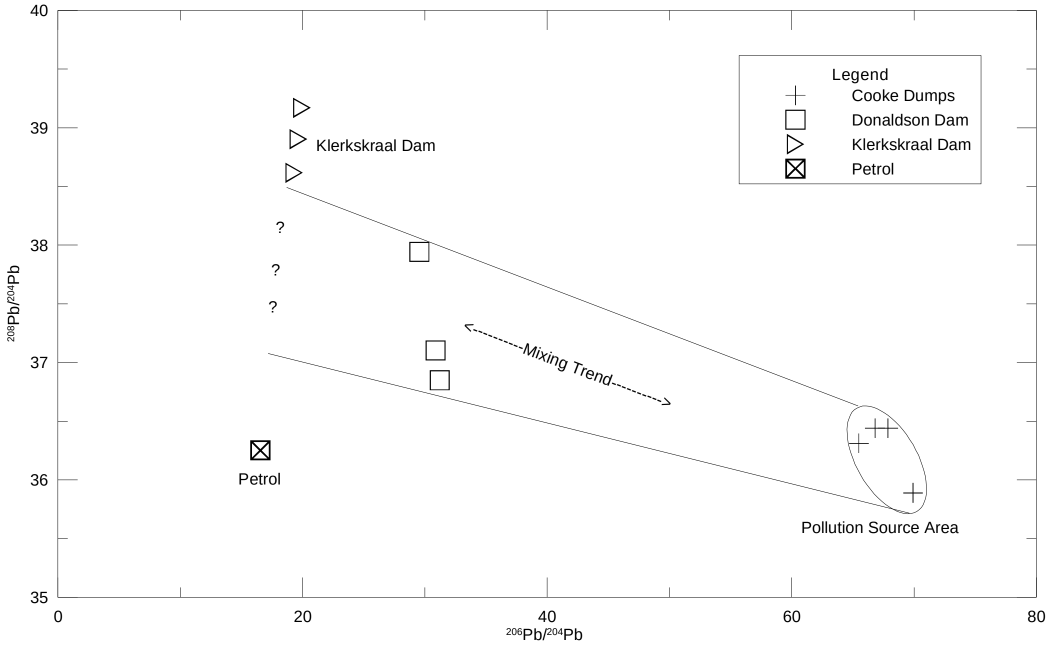


Figure 16. Uranogenic vs. thorogenic lead plot for data collected on mine wastes and sediments from the Cooke Section–Donaldson Dam portion of the catchment.

5.4 Conclusions

Examination of these figures suggests that when using lead isotopes alone, the source of sediment contamination may be determined ot a local scale. It would appear from Figure 14, however, that the method does not give easily understandable results on a regional scale. It is also clear that a better inventory of sources with more analytical data will be needed to identify pollution sources unambiguously.

6 Identification of sources of Wonderfonteinspruit river water using sulphur and strontium isotopes (U. Horstmann and M. Rademeyer)

6.1 General

Seven water samples were submitted by H. Coetzee and G. Ntsume for strontium- isotope analysis of water and sulphur stable-isotope analysis of dissolved sulphate. The samples (about two litres of water each) were presented not filtered or otherwise treated. No sample location or any other description was supplied. For laboratory practical purposes the samples were renumbered (HG1–HG7); Table 1 relates these numbers to the original descriptions.

All sample treatment and preparation was performed in the laboratory of the Council for Geoscience (CGS). Initial sample filtering was assisted by G. Ntsume.

6.2 Sample preparation

Four aliquots (100 to 200 ml) of each sample were filtered through 0,45-μm membrane filters into plastic bottles, using plastic syringes. These splits were used for elemental-concentration analysis, and Sr-, Pb-, O- and H-isotope analysis, and acidified according to analytical requirement.

The remaining bulk of each sample was filtered through a glass vacuum device, again using 0,45-μm membrane filters and acidified (1 ml of conc. HCl for every litre of water). The samples were now ready to be prepared for S-isotope analysis.

The analyte for S isotopes is conventionally SO_2 gas, implying that dissolved sulphate (SO_4^{2-}) from water samples has to be precipitated as $BaSO_4$ before conversion to SO_2.

Precipitation of the soluble sulphate was easily accomplished by adding a 0,5M $BaCl_2$ solution and agitating under slow heating to boiling point. Sulphites (SO_3^{2-}), a result of incomplete oxidation, may also be in the solution thus requiring longer periods to allow for complete precipitation. After allowing sufficient time for the precipitate to settle, the supernatant was aspirated and the sample treated for carbonate.

An amount of 10 per cent HCl was added to the sample, reducing pH to 4, but not less than 3. The sample was allowed to stand for 30 to 60 minutes maximum (^{18}O will begin to equilibrate with atmospheric oxygen) and then heated to boiling point on a hotplate. After settling, the supernatant was aspirated and the precipitate washed several times with deionised water. Excess water was aspirated, the precipitated sample dried at no higher than 80 °C and stored in a small glass vial. The sample was now ready to be converted to SO_2 for stable-isotope analysis.

6.3 S-isotope analysis

The conventional procedure for the measurement of $^{34}S/^{32}S$ ratios in sulphides and sulphates followed presently at the CGS stable-isotope laboratory involves mixing of the sample material with V_2O_5 + SiO_2, combustion of this mixture at ±1 120 °C in an off-line vacuum extraction line and cryogenically trapping the evolved SO_2.

The mass-spectrometric analysis of this SO_2 is done on a semi-automatic, triple collector mass-spectrometer with manual sample change. The analytical principle is a dual inlet system, i.e. the sample gas is analysed relative to a reference gas in an alternating mode.

This whole process is longwinded and time consuming, and access to a more rapid analytical facility is desirable. The environmental isotope laboratory of the Schonland Research Institute at the University of the Witwatersrand, Johannesburg, was recently equipped with a state-of-the-art mass-spectrometer, including peripheral instruments for sample preparation.

The equipment used at Schonland for S- (and C/N-) isotope analysis consists of a GEO 20-20 mass-spectrometer connected to an ANCA–GSL (automated nitrogen and carbon analysis for gases, solids and liquids) sample-preparation system. The principle followed is the coupling of an elemental analyser (ANCA–GSL) to a continuous-flow IRMS (isotope ratio mass-spectrometer, GEO 20-20). This is in contrast to the dual inlet system mentioned above; where dual inlet uses peak-height detection, continuous flow detects and evaluates peak areas.

The S-isotopic composition of the samples was determined using this new method as outlined below. Samples were analysed in duplicate and international standards were used for calibration. The latter reproduced to about ±0,5‰ relative to their accepted values. S-isotope data are given in the conventional δ–notation according to:

$$\delta^{34}S(‰) = \left[\frac{({}^{34}S/{}^{32}S)_{sample}}{({}^{34}S/{}^{32}S)_{s\tan dard}} - 1 \right] \times 1000$$

6.4 Methodology of $\delta^{34}S$ analysis by EA–GC–CF–IRMS (from PDZ Application Note 5)

Samples are dried and ground to a homogeneous mixture. They are then weighed into tin capsules where vanadium pentoxide (V_2O_5) is added to aid combustion. Samples are then loaded into a carousel on the ANCA–GSL. They are then dropped into a furnace held at 1 020 °C where they are combusted in the presence of oxygen. The combusted gases are swept in a helium stream over a combustion and reduction catalyst to purify the gas to sulphur dioxide. Water is removed by a Nafion™ membrane and magnesium perchlorate chemical trap. SO_2 gas is separated from N_2 and CO_2 by a gas chromatograph. The resultant chromatographic peak of SO_2 enters the ion source of the GEO 20-20 CF–IRMS where it is ionised and accelerated. ^{32}S and ^{34}S are separated in a magnetic field then simultaneously measured on a Faraday cup universal collector array. Sample time is normally about ten minutes per sample.

6.5 Sr-isotope analysis

Sr-isotope analyses were carried out in the radiogenic isotope laboratory of the CGS, using conventional cation exchange techniques and mass-spectrometric analysis.

The Sr-isotope ratios are reported in δ–notation as for S (above) using NIST NBS987 with an $^{87}Sr/^{86}Sr$ ratio of 0,71205.

6.6 Results and discussion

Results of the stable-isotope analyses for S and Sr are summarised in Table 27 in the Appendix, and a detailed list of S-isotope duplicate determinations can be found in Table 28. The data for anion and cation concentrations are compiled in Table 29 and Table 30 respectively. Figure 17 illustrates the S-isotopic composition in relation to selected anion and cation concentrations, and Figure 18 shows the isotope ratios of S and Sr in relation to each other and the Sr concentration.

The $\delta^{34}S$ values of the two samples from Donaldson Dam and the 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‰. The difference between these sample groups is further documented by a lesser concentration of Cl^-, Br and B, and a higher amount of K, Mn and Rb in the samples from Donaldson Dam and the River at Donaldson Dam.

With the available information, the S-isotope data of this study are difficult to interpret. This is mainly owing to the lack of "background" values in order to estimate anomalies. The $\delta^{34}SO_4^{2-}$ data from this study are well in agreement with those reported for fresh-water systems worldwide, which lie generally between +5‰ and +15‰ (e.g. Cortecci and Longinelli, 1970; Ivanov et al., 1983). The source for this sulphur can only be speculated on at present. If appreciable anthropogenic pollution can be excluded, the isotopic composition of surface-water sulphate is profoundly influenced by the isotopic composition of rock sulphur it interacted with.

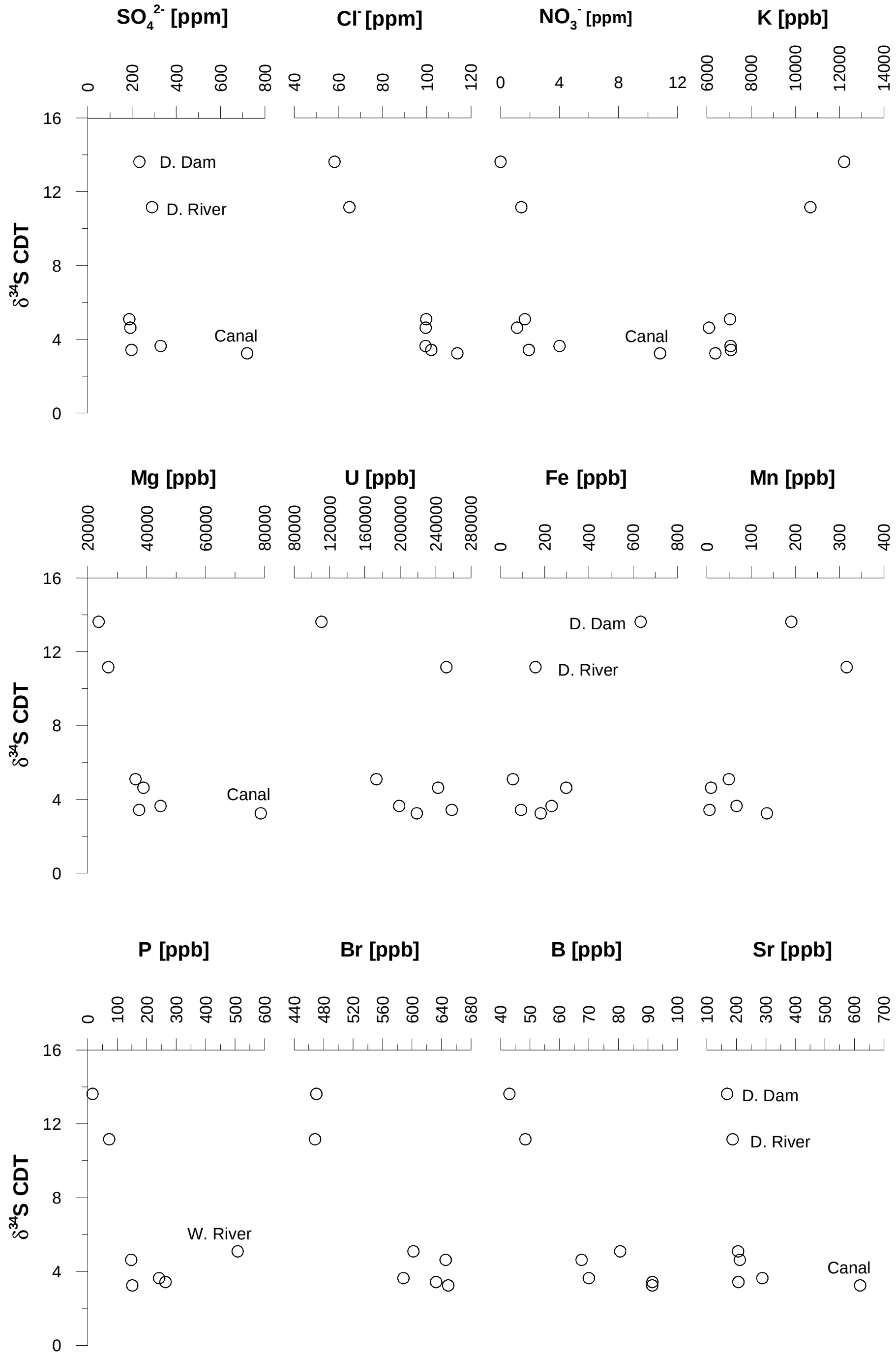


Figure 17. Anion and cation concentrations vs. S-isotopic composition. Note differences in δ^{34}S and elemental contents of the samples from Donaldson Dam and the River at Donaldson Dam, relative to other samples.

Nriagu et al. (1991) estimated the mean $\delta^{34}SO_4^{2-}$ for African rivers to be +2‰ on grounds of an average SO_4^{2-} concentration of <3 mg/l derived mostly from the weathering of Precambrian shield bedrocks. δ^{34}S values of pyrites from the Witwatersrand, however, were found by Hoefs et al. (1968) to lie between 1 ‰ and 4‰, and Smit (2000, see also Horstmann and Bester, 1999) reported pyrites with δ^{34}S ranging from -5‰ to +5‰. In case the sampled waters interacted with such a type of rock, the δ^{34}S values from 3‰ to 5‰ can be explained by oxidative weathering of Witwatersrand sulphides with no or only very little isotope fractionation (e.g. Mitchell et al., 1998).

If the samples from Donaldson Dam and the River at Donaldson Dam also got their S-isotopic signature form their source (recharge?) area, another explanation would be required. δ^{34}S values of 11‰–14‰ are observed in waters which receive input from e.g. groundwaters that leached evaporite rocks and/or other groundwater sulphates with an elevated ^{34}S content. Such isotopic compositions are reported from, e.g., the Amazon Basin and major rivers in Russia (Nriagu et al., 1991), but at much lower SO_4^{2-} concentrations than found in this study. These interpretations, however, would have to be verified by correlations with S-isotope patterns from the relevant catchment areas. It should, however, be borne in mind that the sulphate crusts described in Section 3.5.1 would provide such a source of sulphates, as well as being deposits which preferentially concentrate uranium and other radionuclides.

The SO_4^{2-} concentrations, varying roughly between 200 mg/l and >700 mg/l, point to some different input of sulphur compounds. Similar δ^{34}S values were reported by Horstmann and Eglington (2002) for dissolved sulphates from the Rietvlei Dam, south of Pretoria, but at lower SO_4^{2-} concentrations (25–40 mg/l). As in the case of Rietvlei Dam, anthropogenic pollution sources cannot be excluded and the S-isotopic signatures found there and in this study may point to some kind of anthropogenic source as well. Nriagu et al. (1991) quote the S-isotopic composition of anthropogenic sulphur in general from 0‰ to +10‰, i.e. covering essentially the range of the samples of this study.

Some kind of component mixing is indicated in Figure 17, which illustrates the δ^{87}Sr ratio in relation to the Sr concentration and the δ^{34}S ratio. The conspicuous spread in the δ^{87}Sr values points to some interaction of the water samples with their respective environment. Tentatively, a second-degree polynomial curve with an inverse slope in the range of consideration has been fitted through the δ^{87}Sr vs. δ^{34}S series. This curve yields a $R^2 = 0{,}96$ and can be interpreted as a component/water-mixing curve deduced from the relation of the δ^{87}Sr ratios to the δ^{34}S values of the water samples. A similar relation, albeit in a positive sense, is shown by the δ^{87}Sr ratio plotted against the Sr concentration. This observation is confirmed in a plot of δ^{87}Sr vs. the inverse Sr concentration (Figure 18). Although the sample points are less correlated ($R^2 = 0{,}72$), a rough linear trend emerges, indicating a two-component mixing.

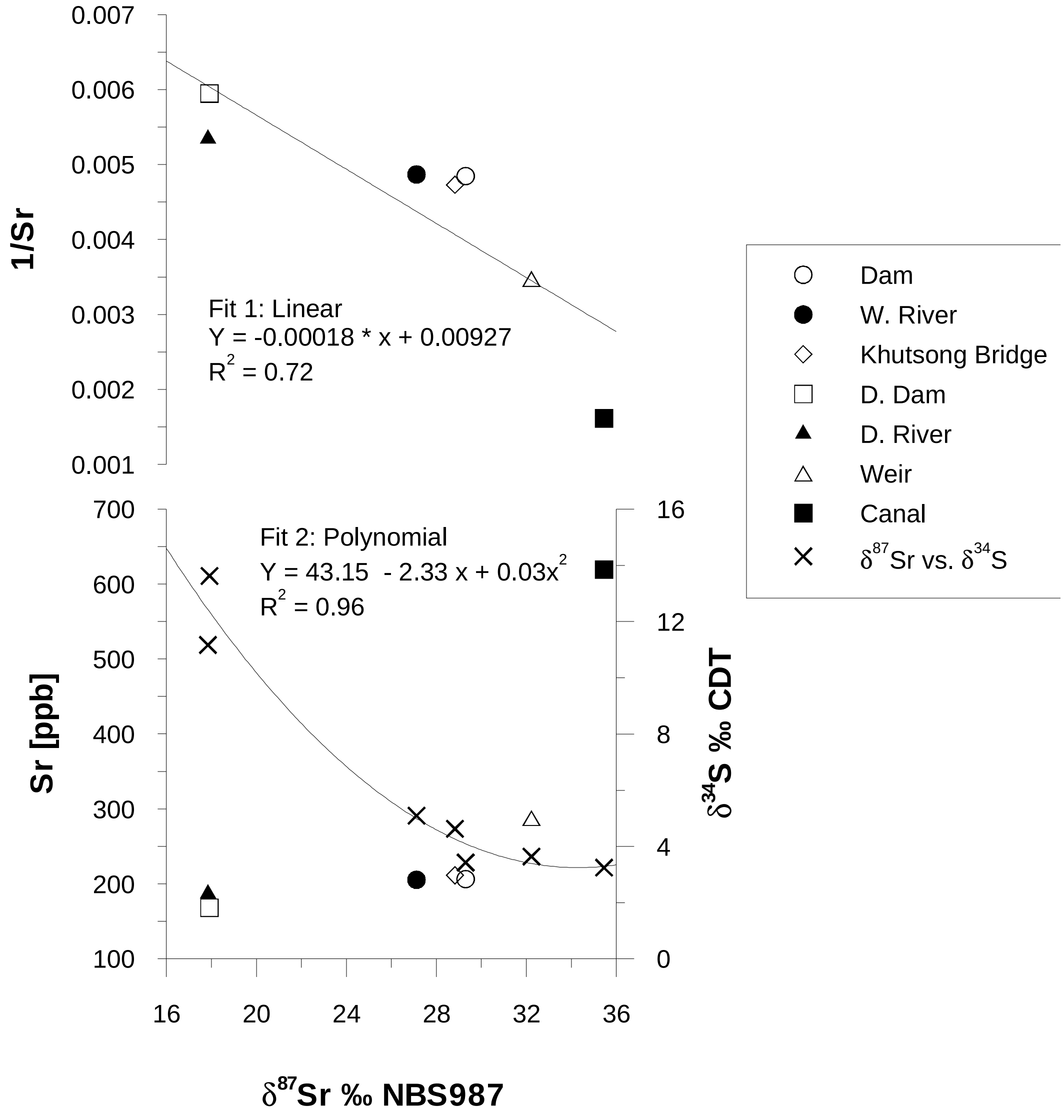


Figure 18. Sr-isotopic composition plotted against Sr concentration and δ^{34}S values. δ^{87}Sr calculated using ^{87}Sr/^{86}Sr of NBS987 = 0,71025.

Such relations can be used to deduce the flow path of water for a particular region or catchment area (e.g. Bullen and Kendall, 1998), but more information about the environment of the sampling sites (like soil, its mineral content, etc.), is required. One possible interpretation would imply that the increasing trend of the radiogenic Sr (higher δ^{87}Sr) with the Sr concentration points to a higher residence time of those samples with more ^{87}Sr. More time was available for chemical reactions and/or leaching to take place, and those waters would become enriched in Sr if suitable rocks/soils are leached and their δ^{87}Sr is likely to increase as well. At the same time, the δ^{34}S values are likely to decrease, as observed, because more isotopically light sulphides (e.g. pyrite) are also leached and the S incorporated into dissolved SO_4^{2-}.

Another and more likely interpretation of the Sr concentration and Sr- and S-isotope patterns is a two-component mixing between mine effluent and water originating from, or having flown through, a dolomite area. This is substantiated by the linear trend of δ^{87}Sr vs. the inverse Sr concentration (1/Sr,Figure 18). Although no end members exist, samples with a low Sr concentration and relatively high δ^{34}S values (Donaldson Dam and River at Donaldson Dam) represent less-contaminated waters. To these waters mine effluent is gradually more admixed as the Sr content increases and δ^{34}S decreases. The inverse (second-order polynomial) correlation curve of the Sr- and S-isotope ratios can thus be explained as a mixing line between "dolomite waters" and effluent. The "dolomite waters" with a lower Sr concentration and higher δ^{34}S values become gradually mixed with mine waters which interacted with isotopically lighter sulphides, and hence lower the S-isotopic composition of dissolved sulphate in the final mix. The relatively high δ^{34}S values of "dolomite waters" most probably originated from the leaching of carbonates from e.g. evaporitic sequences, which is possibly supported by the elevated K content of these samples.

6.7 Conclusion

Sr concentrations, as well as Sr- and S-isotopic compositions reveal the submitted samples to represent two component mixtures most probably of waters originating from dolomite areas with mine effluents. Plots of the strontium-isotopic composition (δ^{87}Sr) vs. that of sulphur (δ^{34}S), as well as of δ^{87}Sr vs. the Sr concentration (normal and inverse), show correlations which are interpreted as mixing lines between the said two components. Although no clear-cut end members can be established, a gradual mixing between waters most probably of dolomitic provenance and mine effluents is indicated.

7 Speciation determination of heavy metals and uranium — BCR Protocol Sequential Extraction (H. Coetzee, M. Rademeyer and G. Ntsume)

7.1 Philosophy of sequential extractions

The philosophy of sequential extraction is that reagents are used in each extraction phase which selectively attack the minerals of interest, allowing the determination of the metal contents (or in this case, the proportion of the total metal content) bound to that phase. Typically, sequential extractions will target those metals bound weakly to the sediment, and those extractable under acidic conditions, reducing conditions and oxidising conditions. Some methods also include initially stripping metals weakly bound to mineral grains and total dissolution of the residue.

The European Union's BCR Protocol sequential extraction method described by Coetzee et al. (1995) was used to determine the metal speciation within the sediments. This method is analytically simpler than the method of Tessier et al. (1979), described by Ure et al. (1993), used previously by Wade et al. (2002) and Coetzee et al. (2002), and excludes the $MgCl_2$ extraction for weakly bound metals. Since this stage has not been found to release significant quantities of any pollutants in either of these studies, the two methods can be regarded as equivalent.

The extraction method used in this study aims to simulate the following environmental conditions:

Table 7. Environmental conditions simulated by the different stages of the BCR Protocol Sequential Extraction

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

7.2 Sample selection

Sequential extractions were carried out on a set of samples collected on the 11th of August 2003. These are the same samples as those used for the XRF study (See Section 4.1.2, Quantitative analytical results determined using X-Ray Fluorescence). The sample localities are listed in Table 4 and presented on

Figure 7.

7.3 Method

1. One gram of sample is weighed out.

2. 40 ml of 0,1 M acetic acid (pH~5) is added to the sample, which is shaken overnight at room temperature. The sample is separated from the solution by centrifuging for 10 minutes at 2 500 rpm and the liquid decanted.

3. The residue is extracted overnight at room temperature with 40 ml of 0,1 M hydroxylamine hydrochloride acidified with nitric acid to pH 2. The sample is again centrifuged for 10 minutes at 2 500 rpm and the liquid decanted.

4. The residue is rinsed in a covered beaker for 1 hour with 10 ml of 30 per cent hydrogen peroxide adjusted with nitric acid to a pH between 2 and 3. The volume is reduced to a few millilitre by heating to 85 ºC. The sample is then rinsed with 50 ml of 1 M ammonium acetate adjusted to pH 2 with acetic acid, and extracted by shaking overnight. The sample is centrifuged again at 2 500 rpm for 10 minutes and the liquid decanted.

5. The three liquid extracts were then analysed by ICP-MS, with quantitative procedures used for Ni, Cu, Zn, As, Cd, Pb, Hg and U, and semiquantitative scans to determine the 70 elements listed in the table below.

In all stages, a total method blank was determined, and the analytical results subtracted from the relevant samples.

The procedure is summarised in Figure 19.

The final stage of the full BCR procedure involves high-pressure microwave dissolution of the inert residue in a mixture of typically hydrofluoric and nitric or hydrofluoric and perchloric acids. Experience within the catchment has shown that the local environmental background levels are very low, compared with the concentrations recorded in contaminated sediments (See the concentrations in samples from Klerkskraal Dam ─ sample W105 in Table 24). It was therefore felt that the significant difficulties in the handling of hydrofluoric and perchloric acids were not justified for this study.

7.4 Data processing

The raw data collected are converted, using the sample masses and extractant volumes, to a total mass of metal extracted (in ng). These masses are then used to calculate the percentage of the total extractable metal per sample for each extraction step.

For purposes of calculation, all values less than zero (*i.e.* less than the total method blank) have been set to zero, and data from samples with low metal concentrations have not been used to construct the plots, as many of the values recorded are approximately the same as the total method blank. The raw data are, however, presented in the tables below.

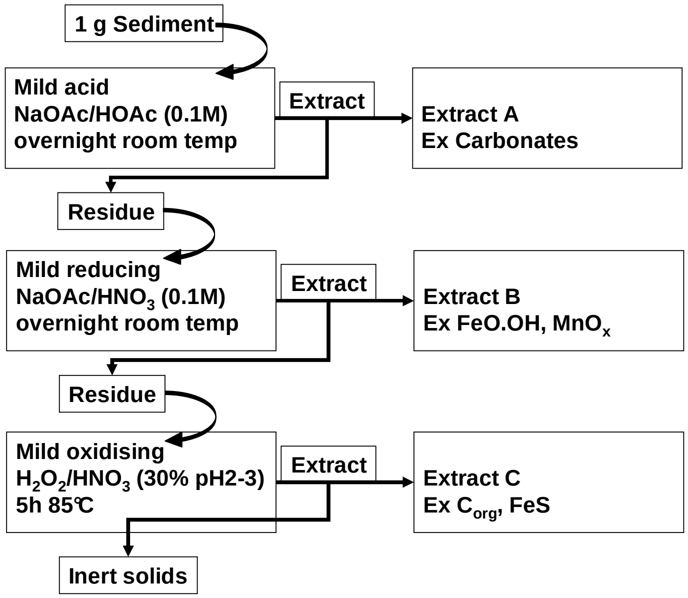


Figure 19. Schematic representation of the BCR Protocol Sequential Extraction procedure used in this study.

7.5 Results

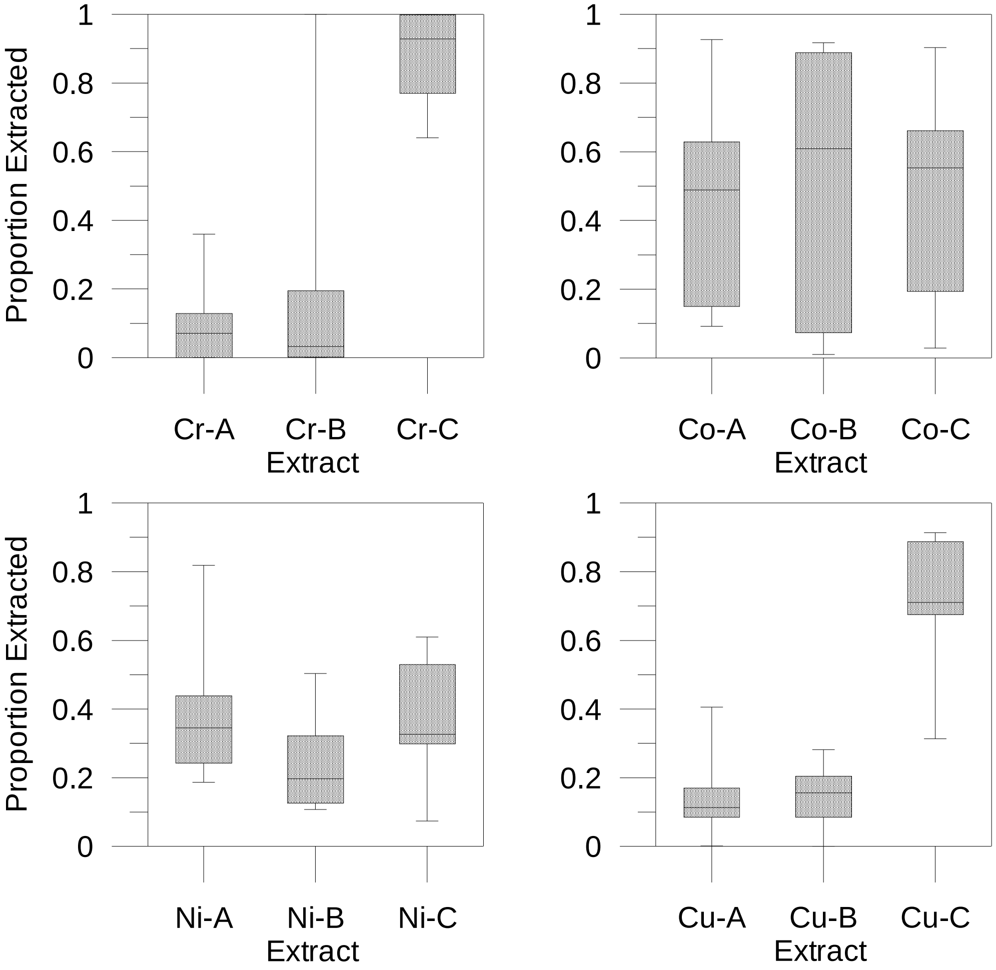
The raw data from the sequential extractions are presented in Table 31 and Table 32 in the Appendix. These have been processed, using the approach described above, to arrive at catchment-wide percentages, the statistics of which are shown graphically in Figure 21. Figure 20 shows the extrema and quartiles of the percentages extracted in each extraction phase for the elements of concern. Barium and lead have also been presented, as radium is likely to follow the chemical behaviour of barium and the total lead results will predict the behaviour of ^{210}Pb.

Two patterns of speciation are seen in the data:

1. Ni, Co and Cd appear to be relatively evenly distributed between the three phases.

2. In Cr, Cu, As, Ba, Pb and U, extract C extracted the largest amount of the element, indicating that most of the metal in the sediment is bound to the reduced (organic carbon and sulphides) phase of the sediment.

In all cases, some of the contaminant metals are bound to each of the three phases identified.


Proportion Extracted
1
0.8
0.6
0.4
0.2
0
Cr-A
Cr-B
Cr-C
Extract
Co-A
Co-B
Co-C
Extract
Ni-A
Ni-B
Ni-C
Extract
Cu-A
Cu-B
Cu-C
Extract

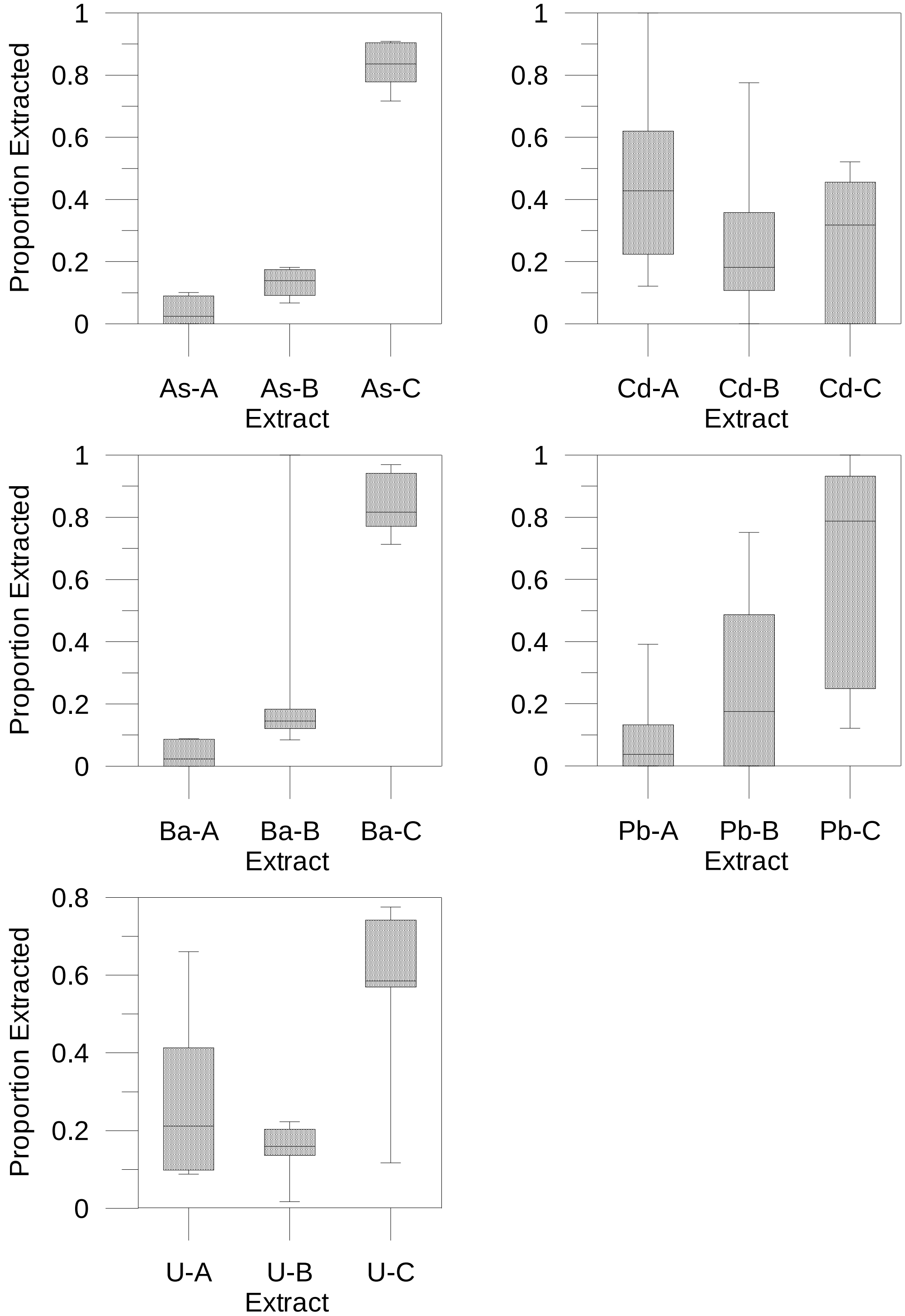


Figure 20. Box and whisker plots showing the distribution of speciation in a selection of samples, for Ni, Co, Cr, Cu, As, Cd, Ba, Pb and U. Extracts A, B and C are the weak acid, weakly reducing and weakly oxidising steps in the BCR Protocol Sequential Extraction

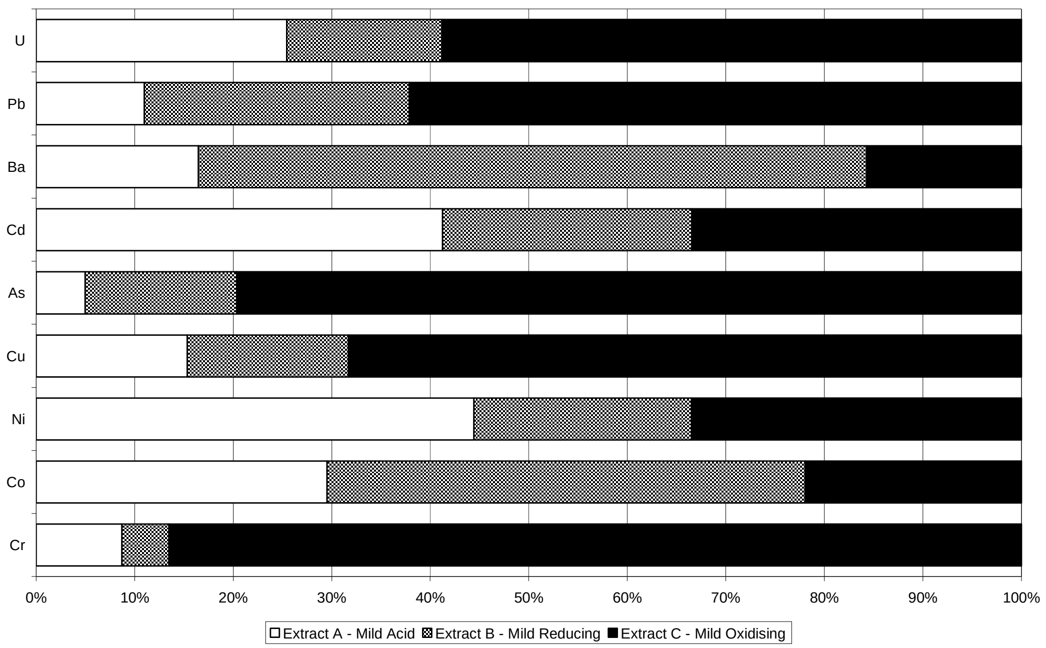


Figure 21. Combined sequential extraction results for Cr, Co, Ni, Cu, As, Cd, Ba, Pb and U.

Figure 21 shows the combined sequential extraction results for all samples. Here, the total metal extracted for each step from each sample has been combined, as if all the samples analysed had been composited. This gives an idea of what effect a catchment-wide environmental event would have. The patterns recorded are similar to those presented in Figure 20.

7.5.1 Discussion

The results presented here show that a significant component ─ generally greater than around 10 per cent ─ of each of the contaminants of interest is bound to each of the three phases attacked in the sequential extraction. This implies that any of the environmental changes mentioned in Table 7 could have a significant environmental impact.

Two distinct patterns are seen in the behaviour of the seven elements analysed for quantitatively. Ni, Co and Cd appear to be distributed in approximately equal proportions between the acid extractable, oxidised and reduced phases, while Cr, Cu, As, Ba (and probably Ra), Pb (including ^{210}Pb) and U are dominantly concentrated in the reduced (susceptible to oxidation) phase. The second group appears to preferentially adsorb onto organic particles or to be included in sulphide grains which form in the sediment owing to bacterial action. Figure 22 shows a backscattered electron scanning electron microscope image of a sample of sediment from Andries Coetzee's Dam. Note the presence of authigenic sulphide ─ probably an iron monosulphide (pers. commun. M. Cloete) ─ with a framboidal habit, typical of the action of sulphate-reducing bacteria and organic material, here in the form of carbon.

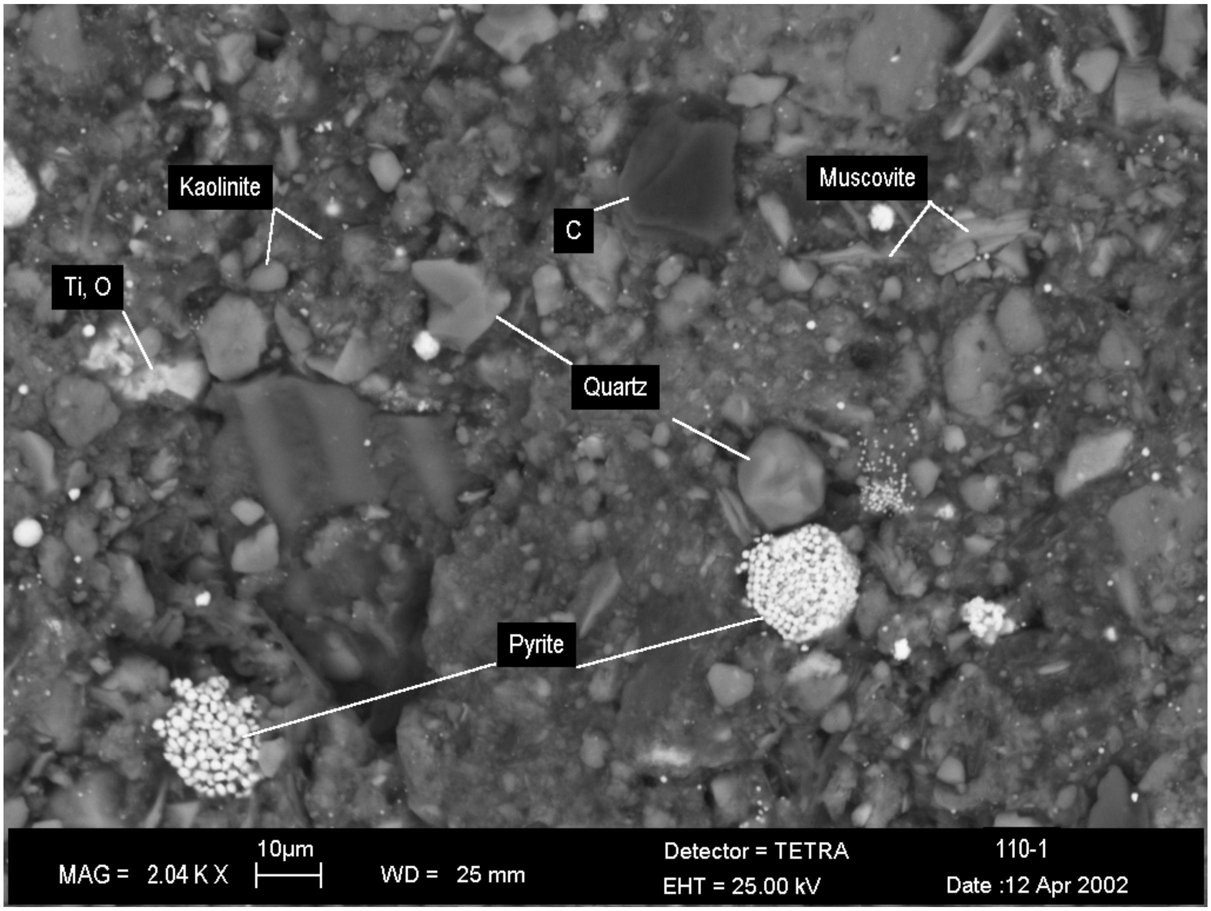


Figure 22. SEM image of a sediment sample from Andries Coetzee's Dam. Note the presence of framboidal iron sulphide[10], and carbon particles.

7.5.2 Implications for understanding the transport of uranium

Within the sediments collected in the catchment, uranium is found dominantly in the reduced phase. The presence of framboidal iron-sulphide grains (See Figure 22) and the absence of transported iron sulphides suggest that the final reduction process occurs in the sediment, most likely by bacterially catalysed reduction of an iron- bearing phase, using carbon as a reductant. The other component of the reduced phase will be the organic component of the sediment, which is significant (see the loss on ignition (LOI) percentages in Table 26). The lack of detrital sulphide suggests that the transport of metals could be by one of three mechanisms:

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

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[10] The pyrite labels in this image are from an initial identification on the SEM, based on the presence of iron and sulphur. Since the crystal structure of the mineral can not be determined in this image, it would be better to simply refer to the authigenic sulphide phase as 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.

The relatively low dissolved-uranium concentrations found by IWQS (1999) (See Figure 2) suggest that transport in one of the particulate phases is most probable. These sediments could then be transported downstream by mechanical processes. The metals bound to the sediments could also be remobilised by oxidation.

7.5.3 Speciation of metals

The results of the speciation study agree with previous studies, showing that the majority of metals are distributed between the carbonate, oxide and reduced phases within the sediment. In this study, the majority of most of the contaminants of concern are bound to the reduced phase of the sediment. This implies that oxidising conditions could remobilise these metals. Future activities in the catchment must therefore either include the removal of the contaminated sediments or must be regulated to ensure that reducing conditions are maintained in the current wetland areas.

7.5.4 Radionuclide and other metal concentrations

A suite of radionuclides have been detected and quantified in a previous study. No radiochemical analyses were performed in this study, owing to cost constraints. Uranium has, however, been measured in a large number of samples, along with a number of other potentially hazardous metal contaminants. In cases where a good chemical analogue exists for a radionuclide, this may be used to predict its behaviour.

Many of the uranium concentrations recorded within the catchment exceed the NNR’s limit for exclusion from regulatory control. The NNR must therefore be called upon to take decisions regarding the nature and scope of regulation for these sediment bodies.

Although South Africa currently has no enforceable standard for sediment contamination, heavy-metal contents in some sediments within the catchment significantly exceed the European Union guidelines.

8 Temporal variation in hydrochemistry of stream water – results of a continuous monitoring study (F. Winde, H. Coetzee and G. Ntsume)

8.1 Method (H. Coetzee)

A '*Hydrolab Quanta water-quality probe*' was installed on the wall of the weir at DWAF monitoring station C2H069, a gauging weir downstream of Welverdiend and upstream of Andries Coetzee's Dam (See Figure 23).

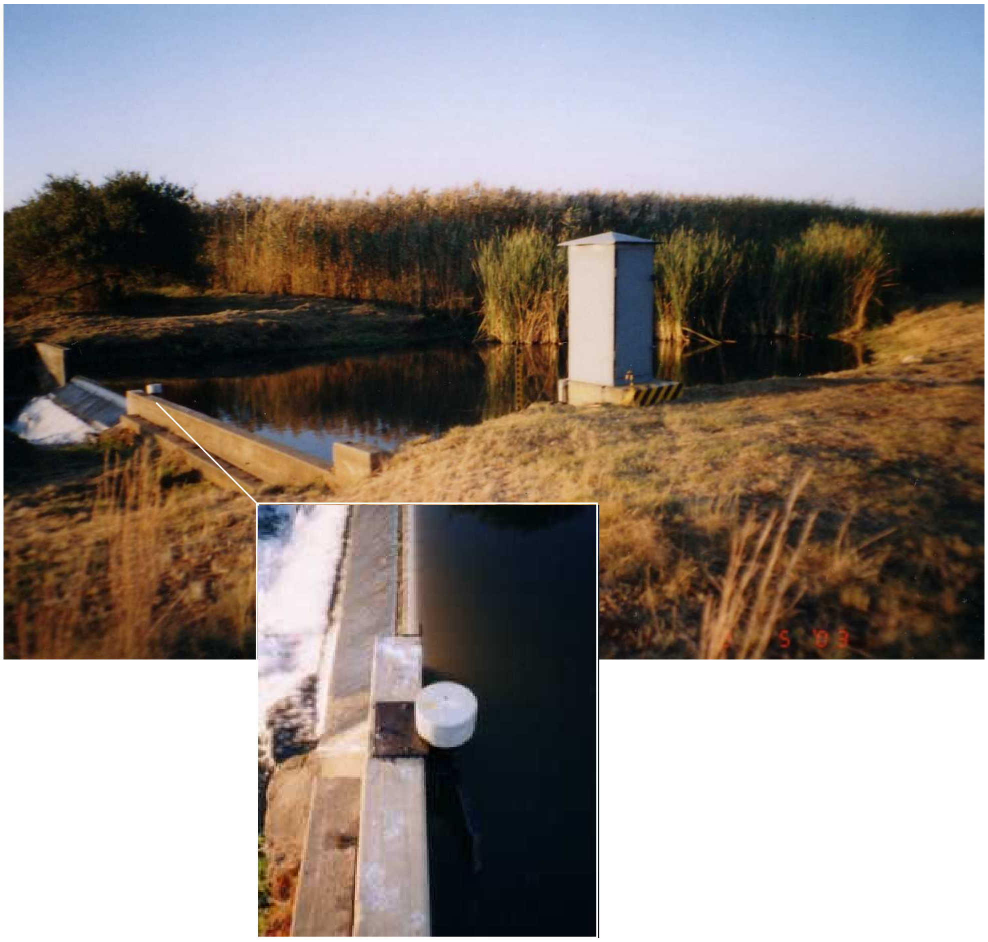

Figure 23. DWAF flow gauging station C2H069 at the Wonderfonteinspruit downstream of Welverdiend. Inset shows position of installed Hydrolab probe at the wall of the weir wired to a datalogger inside the gauging hut from where data were transferred to the Council for Geoscience via a cellular modem (Photos: Winde, 2003)

The unit was fitted with a 'Campbell Scientific Data logger' and cellular modem, to allow remote control and download. The system was powered by a 12V deep-cycle lead-acid battery, which gave a useable battery life of three months. At battery changes, the unit was calibrated using a Hydrolab hand-held controller and standard pH and redox solutions. Owing to initial problems with the installation of the unit, and data communications, the period of measurement was limited to the period from 30 September 2002 to 3 June 2003.

The full parameters of the system are listed in Table 8.

Table 8. Parameters of the continuous-monitoring station

Locality	DWAF station C2H069
Probe	Hydrolab quanta
Parameters measured	Water temperature pH Electrical conductivity (TDS derived from EC) Oxidation-reduction potential (relative to an Ag-$AgCl_2$) cell
Logger	Campbell Scientific with cellular modem
Power source	12 V lead acid battery
Logging frequency	3 minutes for the first two months, thereafter 10 minutes (36 928 measurements)
Measurement period	30 September 2002 to 3 June 2003

A picture of the unit and the hand-held controller is presented in Figure 24.

Figure 24. Hydrolab Quanta Probe (right) and hand-held control unit.

8.2 *Range of parameter variations throughout the measurement period (F. Winde)*

The first step in analysing the temporal dynamic of hydrochemical parameters in the Wonderfonteinspruit is focused on their variation over the entire period. This gives an overview of the range of possible hydrochemical conditions which occurred during this period. Unfortunately this only reflects two thirds of the whole hydrological year, since technical problems caused a data gap of almost four months (June to September 2003). Therefore it is to be expected that the actual annual range of variation might be higher. The number of measurements (counts) and selected statistical parameters are compiled in Table 9.

Table 9. Statistics of stream-water parameters measured in the Wonderfonteinspruit at C2H069 in 3–10-min. intervals over eight months (September 2002–June 2003)

Parameter	Temperature	pH	EC	Eh
Unit	°C		mS/cm	mV (AgCl)
Counts (n)	36 928	36 928	36 928	36 928
Average	19,3	7,80	1,0	620
Median	20,2	7,76	1,0	585
Rel. SD	23%	3%	7%	5%
Min	6,9	6,0	0,6	485
Max	28,6	8,6	1,2	691
Diff Max.–Min. (range)	21,7	2,6	0,7	206
Rel. range [%Max]	76%	30%	55%	30%

As a means to compare variations of different parameters with each other, the relative standard deviation (RSD, also known as variation coefficient) and the relative range (the difference between the maximum and the minimum expressed in per cent of the maximum) are used. Both parameters indicate that the water temperature covers the widest range (76% relative range) followed by the EC (55%). With 30 per cent for both, pH and Eh show significantly lower ranges of ‘long-term fluctuations’ (occurring over the entire period of measurement). The extent of such long-term fluctuations and their possible implications for the uranium transport in the fluvial system are briefly outlined below.

8.2.1 Water temperature

The temperature of stream water at weir C2H069 ranges from 7 to 29 °C. Since three winter months were not measured (June–August 2003), it is likely that the annual minimum is lower than 7 °C, resulting in an even higher annual range. Relevant implications of temperature fluctuations on the aqueous transport of uranium include:

- Changes in solubility of dissolved gases such as CO_2 and O_2, which in turn may affect the pH and Eh of the water

- Shift of temperature-dependent dissociation equilibria that may affect the EC.

8.2.2 pH-value

With pH-values from 6,0 to 8,6, stream water at this point in the longitudinal profile of the Wonderfonteinspruit varies only moderately ranging from weakly acidic to moderately alkaline conditions.

Although it is mathematically incorrect to calculate an arithmetic mean for logarithmic values such as the pH, the resulting average pH of 7,80 suggests that alkaline conditions dominate throughout the measurement period in the Wonderfonteinspruit. While this might only result from some extreme alkaline pH-peaks shifting the average upward, it is also supported by the median, which indeed is a better indicator of what conditions actually prevail. In this case the median of the almost 37 000 data is 7,76, indicating that alkaline conditions occur for at least 50 per cent of the time (Table 9).

It should, however, be noted that the relatively high level of pH is not constantly present, but largely the result of daily peaks caused by photosynthesis. These diurnal pH oscillations of the stream water are analysed separately.

With a range of 2,4 pH-units over the measuring period, the H^+-concentration in the Wonderfonteinspruit fluctuates by more than a 100 times. This may have effects on the mobility of uranium, as discussed earlier.

8.2.3 Electrical conductivity (EC)

The EC of the Wonderfonteinspruit at C2H069 fluctuates over the eight-month period between 0,7 and 1,2 mS/cm. An average of 1,0 mS/cm and a close-by median of 0,99 mS/cm suggest that the EC, most of the time, remains in the upper half of the range. While low EC values occur only sporadically after rainstorms (dilution effects), high EC levels, in general, last longer.

Being a lump parameter for the concentration of dissolved solids such as sulfates, chlorides, etc., the EC is commonly used as an indicator for waste-water impacts. In terms of uranium transport it indirectly indicates the presence of potential binding partners for uranium such as sulphates, carbonates and phosphates to form inorganic uranyl complexes.

High EC values may also indicate reduced adsorption of uranium onto potential sorbents due to binding competition by other dissolved cations such as Na, Ca, etc.

8.2.4 Redox potential (Eh)

With values ranging from 274 mV to 480 mV (converted into H^+-standard electrode scale), the redox potential in the Wonderfonteinspruit at weir C2H069 is oxidising throughout the measuring period. Together with the pH as the other mater variable, the redox potential largely controls not only speciation and solubility of uranium but also the intensity and rate of many precipitation processes known to immobilise uranium and other heavy metals.

8.3 Dynamics and patterns of temporal variation (F. Winde)

While the afore-mentioned range of temporal variation indicates the extent to which the measured parameters may fluctuate in the Wonderfonteinspruit, it does not allow for discerning patterns of such fluctuations as an indicator for possible causes of the temporal variations. In the following the temporal dynamic for each parameter is analysed with regard to its seasonal, diurnal and event-related fluctuations. Owing to the wide variety of possible events and their different impacts on the parameters, event-related fluctuations are dealt with separately.

8.3.1 Water temperature

Seasonal fluctuations

The eight-month time series of the water temperature in the Wonderfonteinspruit at station C2H069 suggests diurnal and seasonal patterns superimposed by response to events such as rainstorm and waste-water discharges (Figure 25).

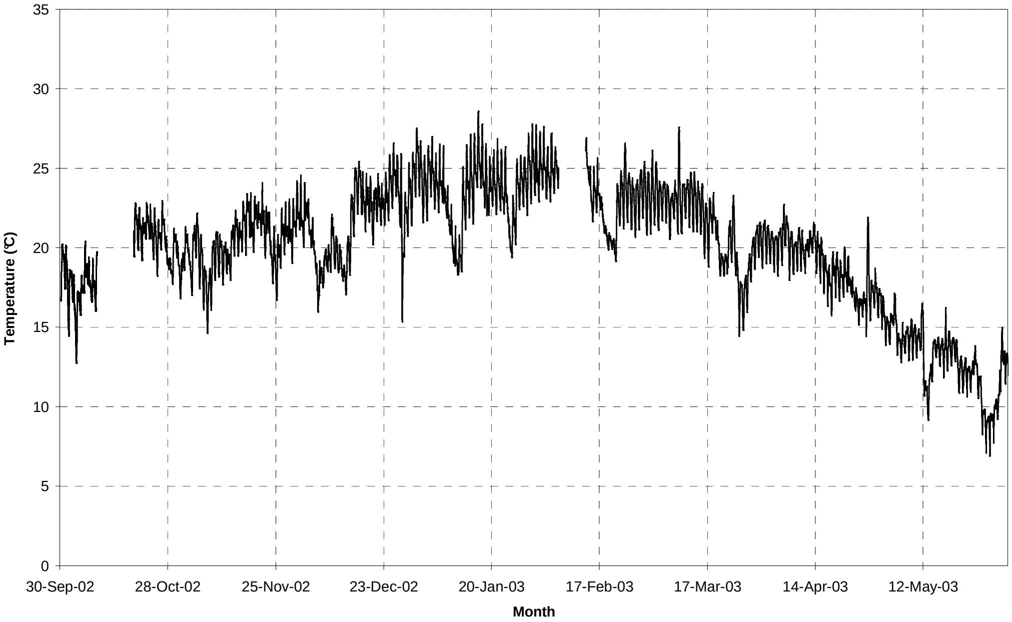

Figure 25. Temperature variation for the measurement period

Using monthly data of average minima and maxima, the seasonal variation of the stream-water temperature becomes clear, being warmest in the summer months and colder in the winter months (Figure 26).

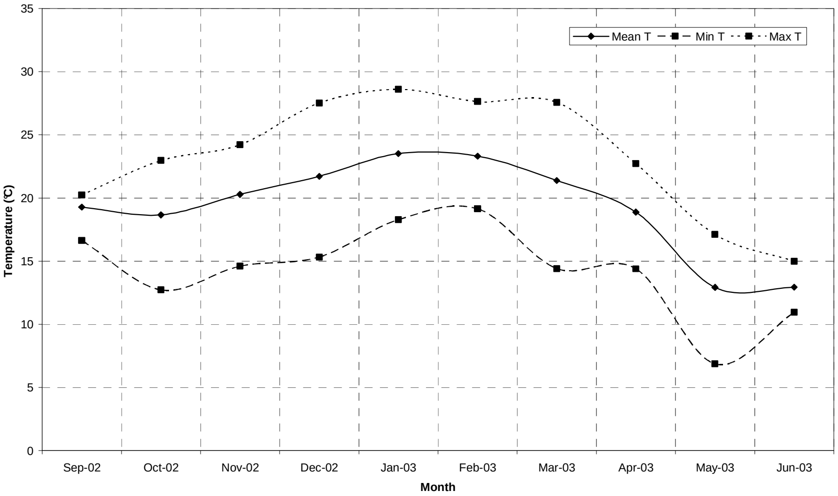

Figure 26. Monthly average and extremes (min. and max.) of water temperature (Tw) in the Wonderfonteinspruit, based on 10-min. data measured at station C2H069 from 30 September 2002 to 03 June 2003

The absolute maximum temperature was measured in December 2002, with the highest monthly average in January 2003. The absolute minimum temperature was measured during May 2003, which was also the month with the lowest average temperature. The fluctuations follow normal seasonal variations in solar-radiation intensity and duration.

Looking at the extent of monthly temperature fluctuations expressed as range relative to the maximum of the respective month, no clear seasonal pattern is discernable (Figure 27).

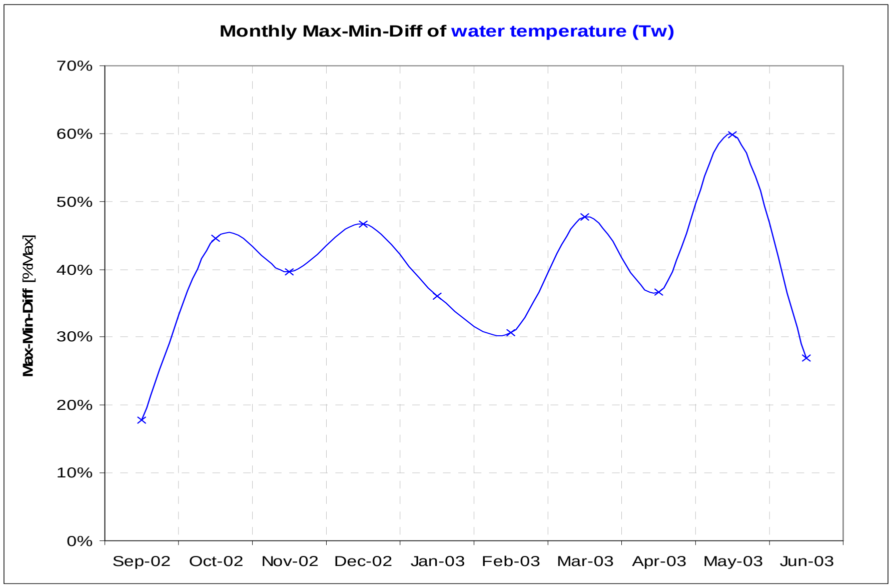

Figure 27. Extent of monthly fluctuations of the water temperature in the Wonderfonteinspruit at DWAF station C2H069 between September 2002 and June 2003, depicted as difference between monthly maximum and minimum (range) expressed in % of the monthly maximum

The highest temperature fluctuations occurred in autumn (May 2003) and the lowest in summer (February 2003). Increasing day–night temperature differences in autumn as a transitional season, where air temperatures during the day are still warm while nights are already becoming increasingly colder, might cause this. The fact that this is not reflected in high fluctuations during September (spring) is manly due to the low number of measurements in that month.

Diurnal variations

In addition to seasonal variation, the water temperature also displays pronounced diurnal oscillations, which are mainly (but not exclusively) caused by daily cycles of solar–radiation intensity (Figure 28).

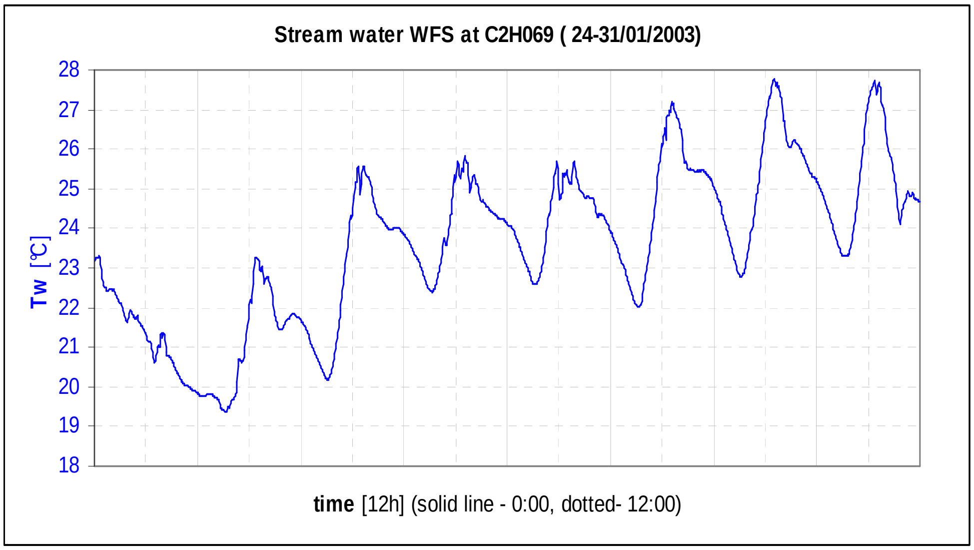

Figure 28. Diurnal oscillations of stream-water temperature in the Wonderfonteinspruit in summer (note: T-max. occurs during the afternoon)

The water temperature fluctuates between 3 K/d in winter and 5 K/d in summer.

The daily minimum commonly occurs between 8h00 and 10h00 (Figure 28), while the temporal occurrence of maxima varies considerably. In summer they are commonly reached in the afternoon (14h00–17h00) (Figure 28), while in winter maxima occur late at night (22h00–0h00) (Figure 29).

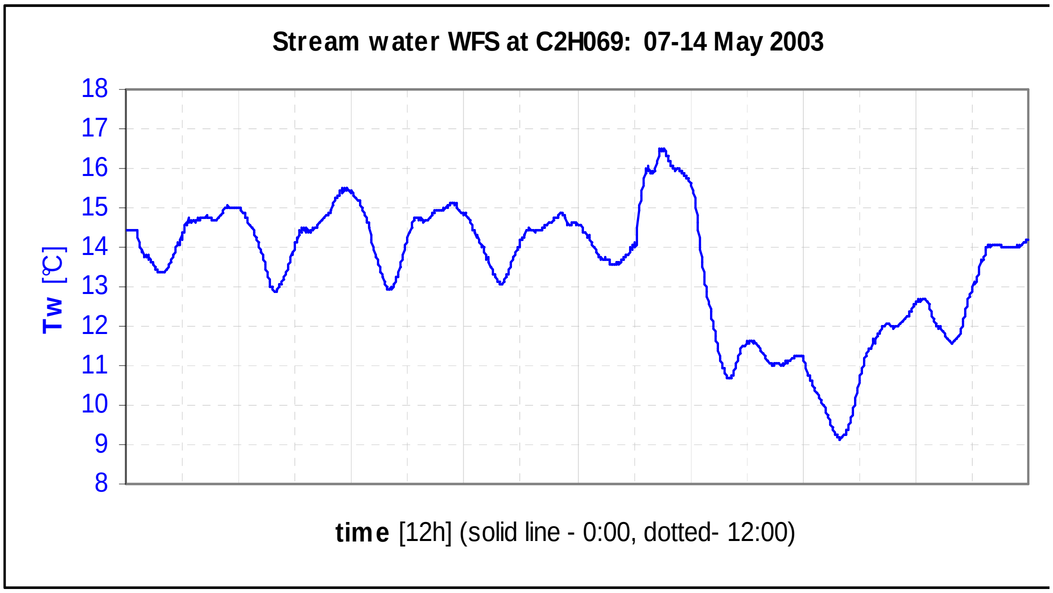

Figure 29. Diurnal oscillations of stream-water temperature during a typical winter period (Note: T-max. frequently occurs during night time)

Such late-night maxima were also found at the Koekemoerspruit, caused by discharge of fissure water from underground mine workings (Winde, 2002).

Originating from 1 300 m below surface and being subjected to the geothermal gradient, this water reaches the surface with an elevated temperature. In winter, therefore, it frequently is considerably warmer than the water in the receiving stream. With higher discharge rates after hours, the input of a large volume of warm fissure water results in the observed late-night temperature maximum.

A similar situation seems to exist at the Wonderfonteinspruit which has an impact on the diurnal dynamics of the stream-water temperature. A ‘shoulder’ in the temperature graph, indicating an interruption of the daily cycle, points to the discharge of warmer-than-stream fissure water (Figure 30).

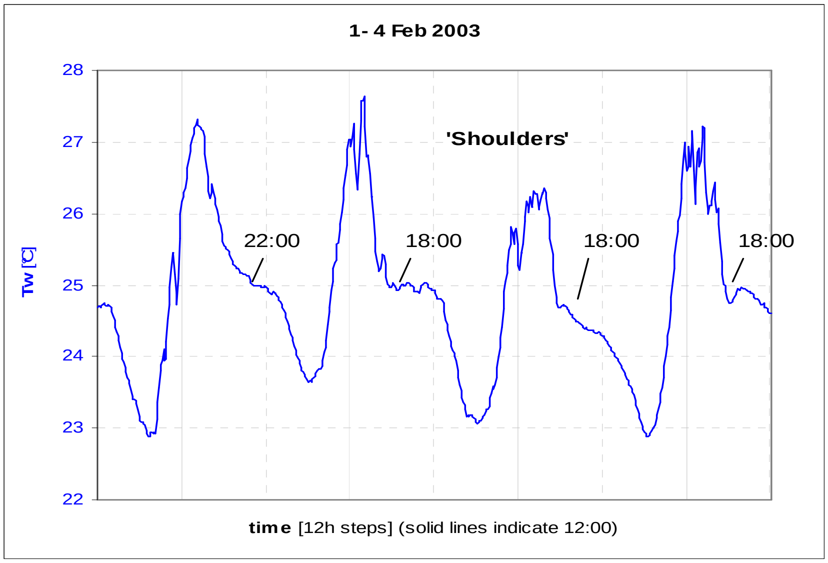

Figure 30. Modifications of the temperature cycle in the Wonderfonteinspruit supposedly caused by the discharge of warmer-than-stream fissure water interrupting nocturnal temperature decrease, as it is indicated by ‘shoulders’ on the right-hand side of the daily graph (1–4 February 2003). The time given indicates the start of the shoulder occurrence.

This is supported by the fact that these shoulders occur at a more or less fixed time of the day that might relate to lower electricity tariffs.

8.3.2 pH-value

The pH time series of 10-min. data shows that short-term fluctuations occur within a rather narrow range between 7,5 and 8, with some exceptions exceeding this range in summer (Dec 2002–Jan 2003) and early winter (April 2003) (Figure 31).

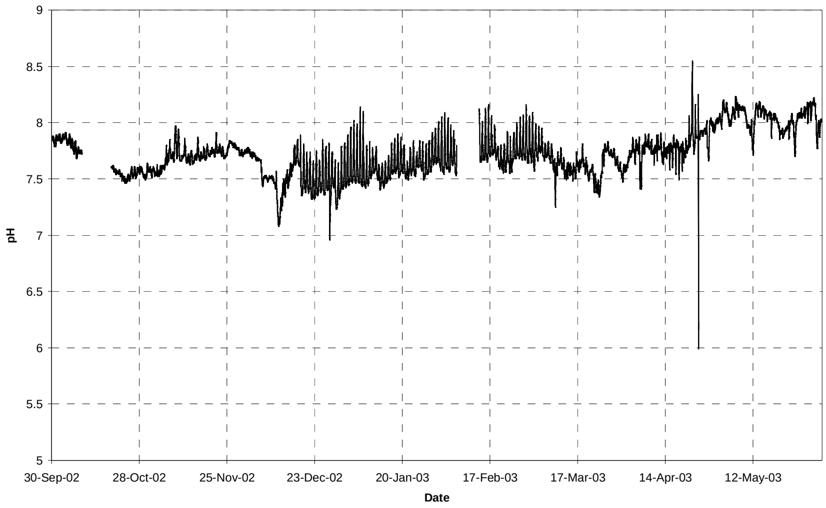

Figure 31. pH variation for the measurement period

While no clear seasonal pattern is discernable at first sight, pronounced diurnal oscillations occur during spring (September–October) and summer (December–January). Thereafter the diurnal oscillations transform into rather erratic fluctuations.

Seasonal variations

While the 10-min. data suggest almost no seasonal fluctuations of the pH, time series of monthly averages and extrema show a slight decrease of average minima and maxima throughout the summer months. All three statistical parameters are at their lowest level in December (Figure 32).

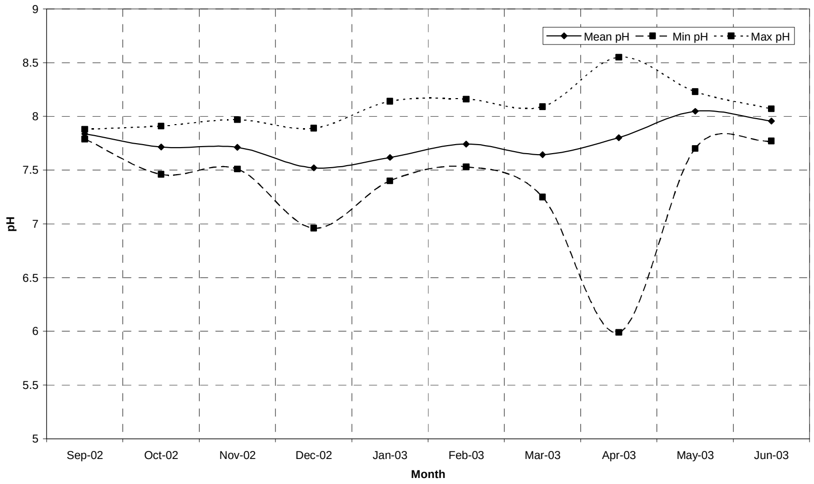

Figure 32. Monthly average and extremes (min. and max.) of the pH-value in the Wonderfonteinspruit, based on 10-min. data measured at station C2H069 from 30 September 2002 to 03 June 2003

With the highest maximum and lowest minimum both occurring during April 2003, this is the month with the most pronounced pH-fluctuations, followed by December 2002 (Figure 33).

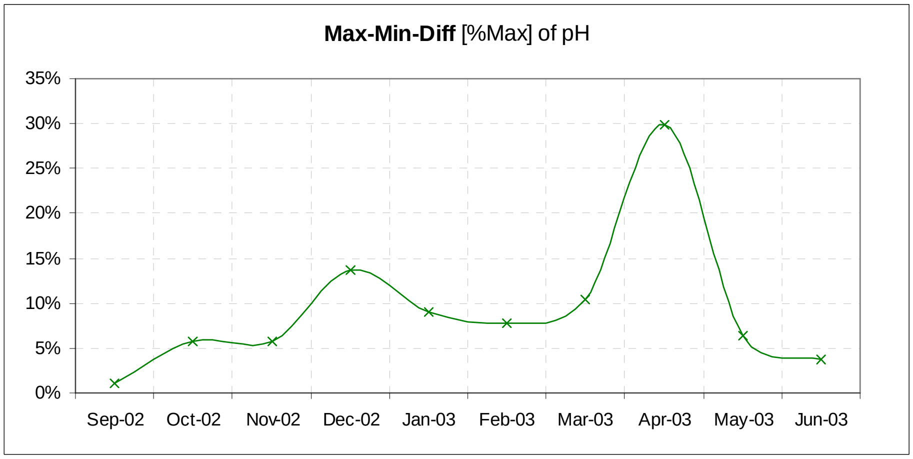

Figure 33. Extent of monthly fluctuations of the pH in the Wonderfonteinspruit at DWAF station C2H069 between September 2002 and June 2003, depicted as difference between monthly maximum and minimum (range) expressed in % of the monthly maximum

This, however, is hardly a seasonal effect, since the extreme pH-range in April is caused by two single events leading to a maximum of 8,5 and a minimum of 6,0. The higher range of pH in December is mainly due to the low minimum pH caused by an increased input of acidic rainwater during convectional summer rains. The associated drop in pH of the stream water is discussed in connection with the analyses of event-related fluctuations.

Diurnal variations

Pronounced diurnal variations are largely confined to the vegetation period in summer (December–February) owing to the action of photosynthetic water plants, phytoplankton and algae. During summer the pH starts to rise in the early morning, around sunrise, and reaches a peak value around midday before dropping through the afternoon, as the intensity of solar radiation and therefore photosynthetic activity decreases. The pH remains at its minimum level during the night when no sunlight for photosynthesis is available (Figure 34).

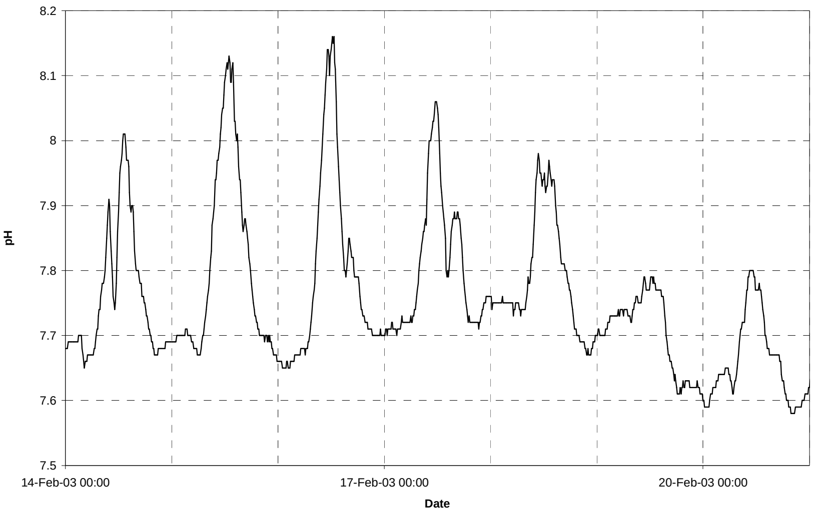

Figure 34. Typical diurnal pH variation in summer

The magnitude of this variation has a mean value of around 0,3–0,4 pH units, with a maximum of around 0,5–0,6 units in February.

8.3.3 Electrical conductivity

Electrical-conductivity values for the measurement period are shown in Figure 35.

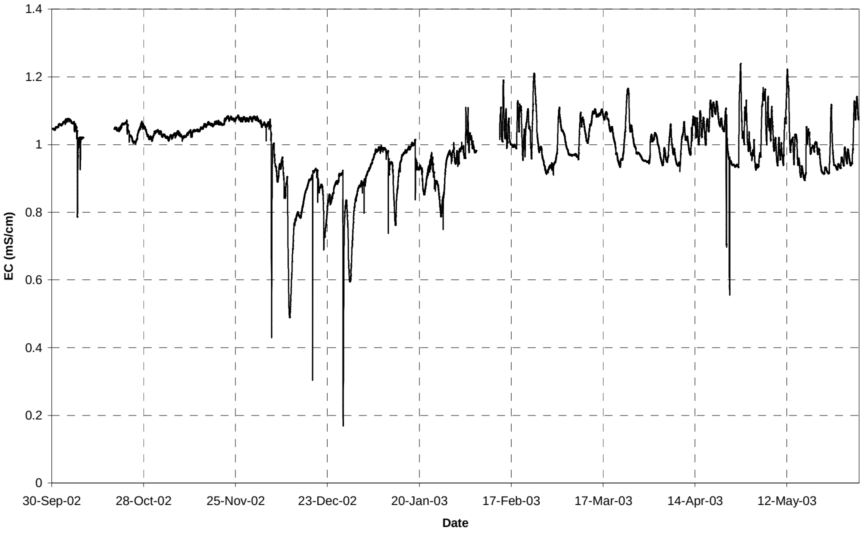

Figure 35. Electrical-conductivity variation for the measurement period (3–10-min. data)

The time series of 10-min. data displays pronounced short-term fluctuations superimposing a long-term decrease during summer. In how far the short-term fluctuations follow diurnal cycles, and whether the long-term trend in summer is a seasonal effect are analysed in the following.

Seasonal variations

Monthly averages show a decrease in conductivity during the summer months, mainly due to dilution of the river water with clean rainwater (

Figure 36). Individual rainfall events are seen as the sharp downward spikes in the data.

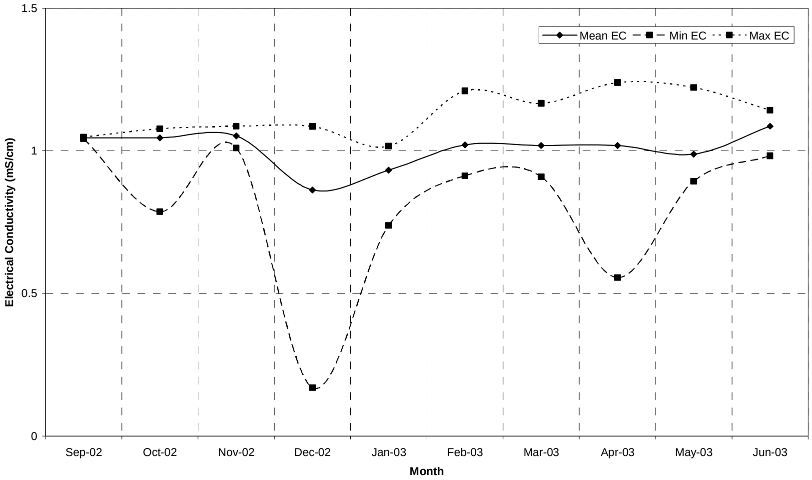

Figure 36. Monthly average and extremes (min. and max.) of the EC in stream water of the Wonderfonteinspruit, based on 10-min. data measured at station C2H069 from 30 September 2002 to 03 June 2003

Similar to the pH, the EC shows the highest monthly fluctuations in December 2003 and April 2003 (

Figure 37).

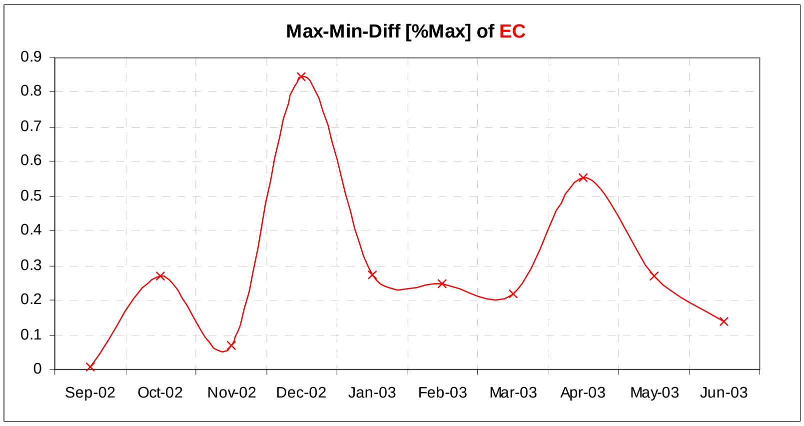

Figure 37. Extent of monthly fluctuations of stream water EC of the Wonderfonteinspruit at DWAF station C2H069 between September 2002 and June 2003, depicted as difference between monthly maximum and minimum (range) expressed in per cent of the monthly maximum

Identical processes also cause monthly variations, namely:

- high rainfall volumes in December leading to the dilution of the polluted stream water and an associated drop of EC (
- Figure 37)
- two events in April leading to an EC increase, which points to discharge or spillage of waste water into the stream.

Diurnal fluctuations

In order to trace possible diurnal oscillations of the EC, a period was chosen in which all other parameters showed pronounced daily variations. However, no diurnal fluctuation could be found for the EC (Figure 38).

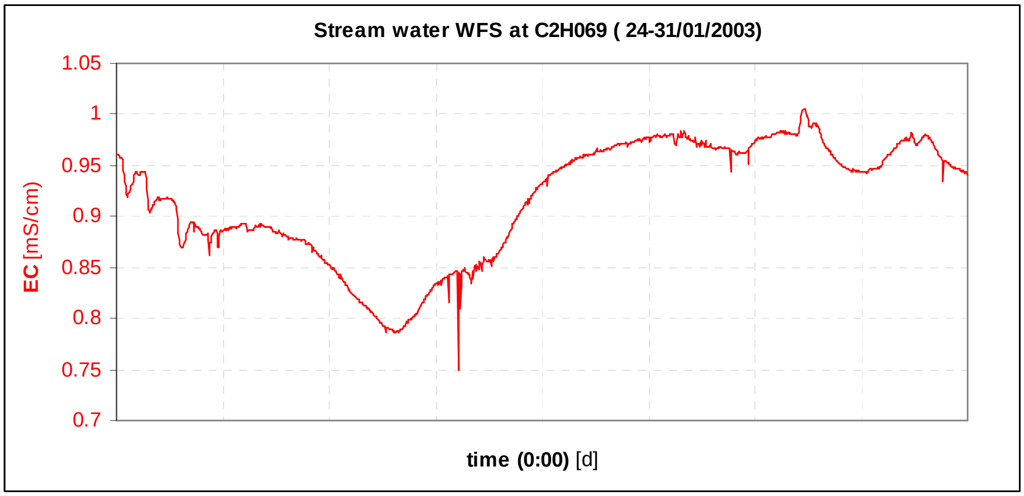

Figure 38. EC of an eight–day period in January 2003 where all other parameters show distinct diurnal oscillations displaying no regular daily pattern

Instead, sharp short-term drops of the EC point to rain storms as a major factor governing the dynamics of the EC (Figure 38). Possible causes for the longer-lasting drops discernable in Figure 38 are discussed in connection with event-related fluctuations.

8.3.4 Redox potential (Eh)

The 10-min. interval-based times series of the Eh displays distinct and frequently occurring short-term fluctuations superimposing a long-term trend of increase from approximately 300 mV to a plateau of about 400 mV (Figure 39).

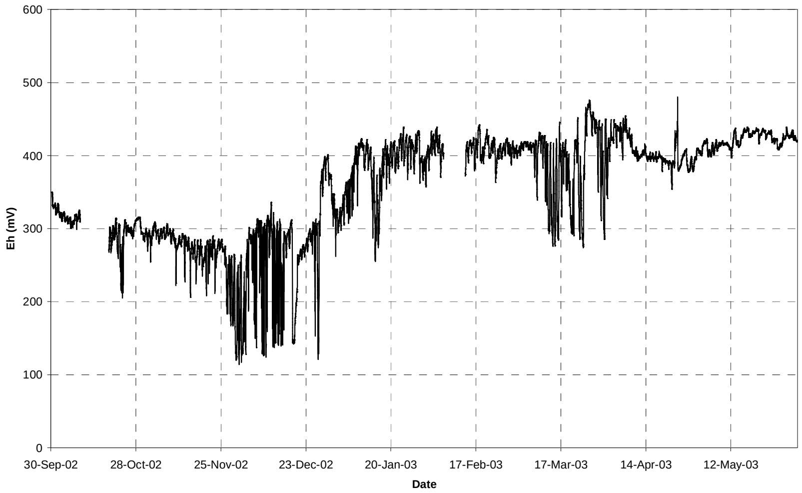

Figure 39. Eh variation for the measurement period

Seasonal variations

Redox-potential values show a steady decrease until December, followed by a large increase during the summer months onto a stable plateau (Figure 40).

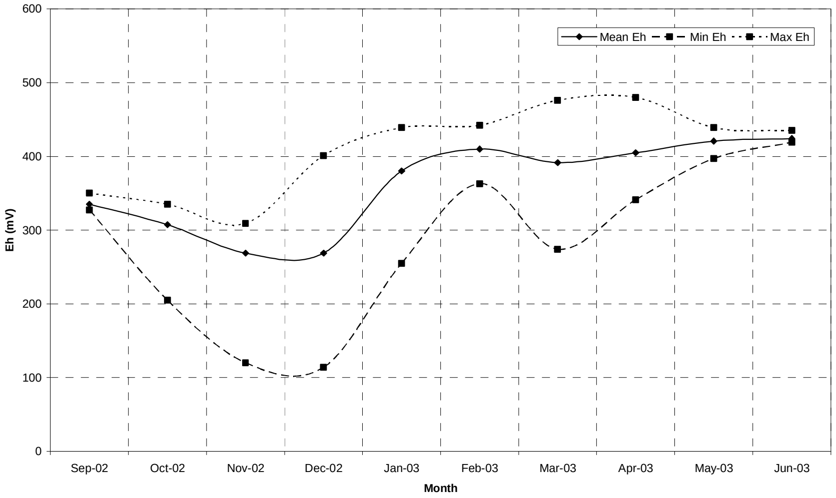

Figure 40. Monthly extrema and mean Eh values

The most likely reason for this increase is the introduction of oxygenated water with summer rainfall.

Similar to the pH and EC, the largest monthly variability occurs in December and autumn (March) (Figure 41). The large variability in December is most likely due to flushes of material into the river by thunderstorms, causing low minima (sewage overflows) as well as high maxima (rainwater run-off) (Figure 40).

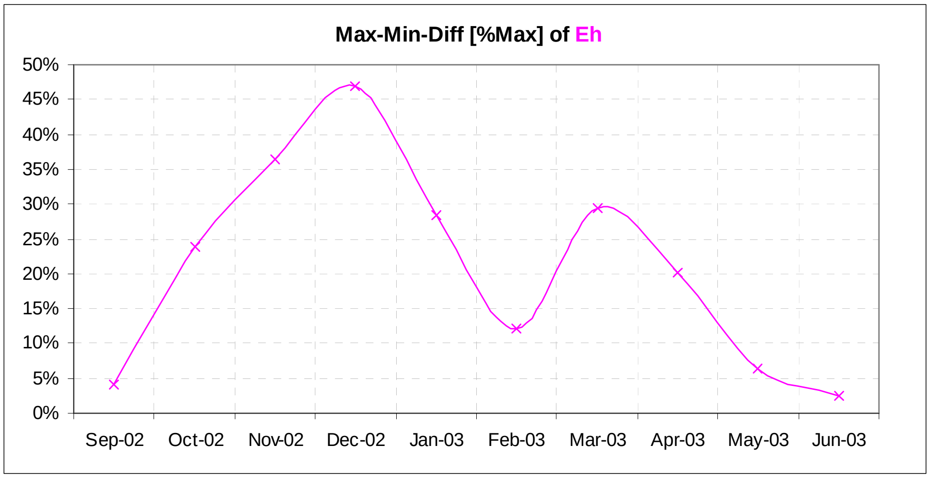

Figure 41. Extent of monthly fluctuations of stream-water Eh of the Wonderfonteinspruit at DWAF station C2H069 between September 2002 and June 2003, depicted as difference between monthly maximum and minimum (range) expressed in per cent of the monthly maximum

With regard to Eh maxima, responses of the Eh to sudden pH-drops due to acidic rainwater are also to be considered, as the Eh reacts inversely to the pH.

Diurnal variations

Diurnal oscillations of the Eh are particularly pronounced in summer (Dec.–Jan.), while later in the year a more erratic pattern of fluctuations seems to dominate. An example for a typical summer period is shown in Figure 42.

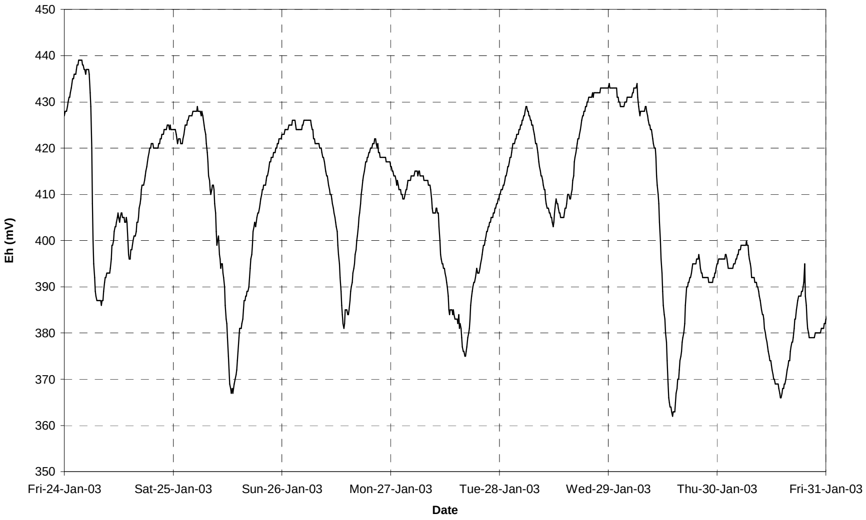

Figure 42. Diurnal fluctuations in Eh during the period 24–31 January 2003

In contrast to the pH and temperature, the Eh rises during the night to a maximum occurring around midnight and drops during the day to the daily minimum around noon. It inversely reflects the dynamic of the pH with which it is closely associated. The daily fluctuations range from some 50 mV/d to 130 mV/d.

In addition to this the Eh displays frequent drops, which do not seem to have any periodicity but were also observed in other streams (Winde, 2003). It is suspected that they are the result of instrument-related processes rather than natural causes. Eh-measurements are by their nature rather difficult to take, since probes in general show distinct delays in responding to Eh changes in the measured medium. It is suspected that these delays might lead to a build-up of some kind of potential within the instrument which then is subsequently released, resulting in re-occurring sharp drops.

8.4 Relationships and interactions between measured parameters (F. Winde)

In order to understand driving forces behind the temporal dynamic of the stream, chemistry analyses of interactions between the different parameter are analysed using monthly-average-based time series and 10-min. interval-based charts.

8.4.1 Parameter interactions based on monthly-average time series

Water temperature — pH relation

The time series of monthly-average values of both parameters are shown in Figure 43.

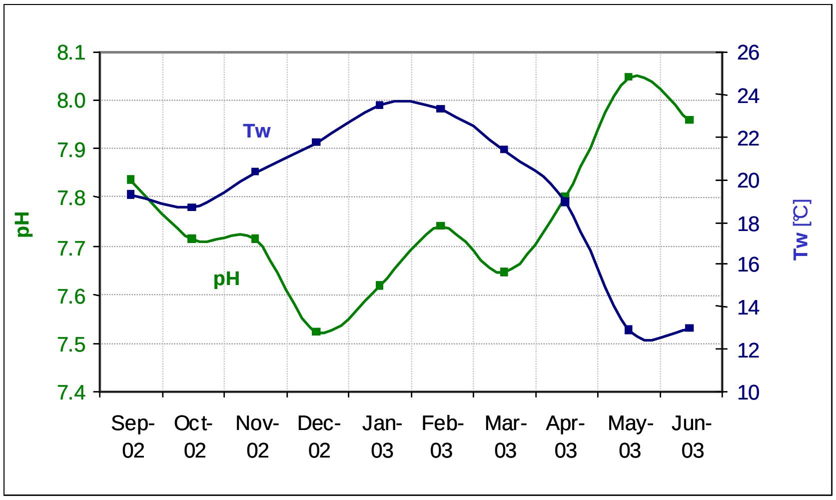

Figure 43. Relation between water temperature and pH in the Wonderfonteinspruit, based on monthly-average values

Figure 43 suggests an inverse relation between water temperature and pH, with high temperature values during summer coinciding with low pH values, and decreasing temperature matching with increasing pH in winter. A possible explanation for this somewhat unexpected relation might be acidic rainfall that lowers the pH at a time when solar radiation increases the water temperature. Cooling down in winter and receiving significantly less rain, the water temperature drops while the pH recovers aided by a higher proportion of alkaline dolomitic water in the stream.

Water temperature — EC relation

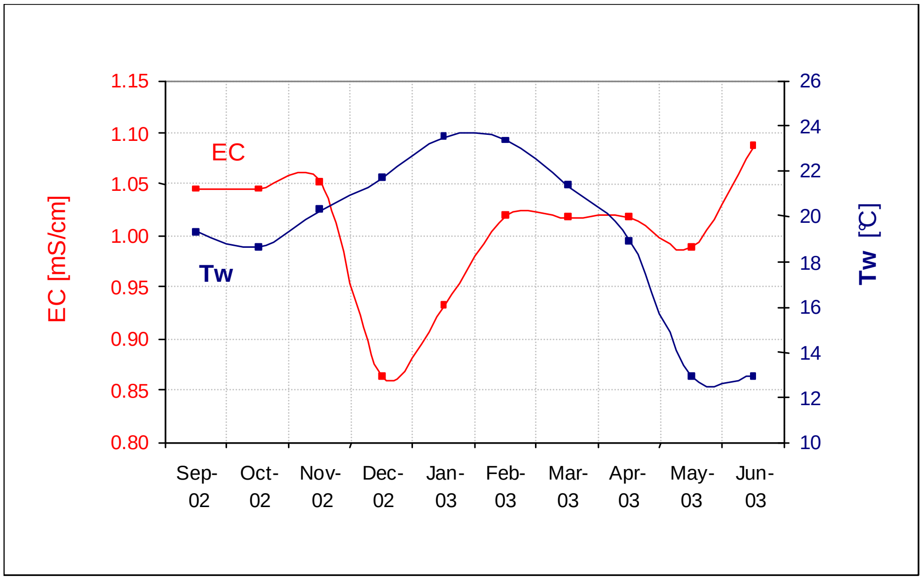

Figure 44. Relation between water temperature and EC in the Wonderfonteinspruit, based on monthly-average values

Since temperature increases the mobility of free ions in a solution, its simultaneously rising temperature results in an increasing EC. For this reason the effect of water temperature needs to be compensated for before comparing EC values from different solutions. Normalising EC measurements electronically to a ‘reference temperature’ of 25 °C or 20 °C respectively commonly does that. Since all EC measurements in this study were taken by a temperature-compensated probe, those impacts of temperature on EC are not relevant.

However, water temperature also has an impact on dissociation and solubility of many chemical compounds, resulting in increased concentration of dissolved solids at higher temperatures. Such a direct relation between EC and water temperature, however, was not found. Instead, time series of both parameters based on monthly averages show, if any, a weak inverse relation where the highest EC occurs in winter at low water temperatures (May–June) and decreases in summer when water temperature is high (December and January).

Contradicting the actual physical relationship between the two parameters, it is likely that again — as found with the relation between pH and water temperature — impacts of third factors on one or both parameters actually govern this relation. In this case low monthly-average EC values might only coincide with high temperatures during the summer months owing to higher volumes of low-EC rainwater entering the system.

pH–Eh relation

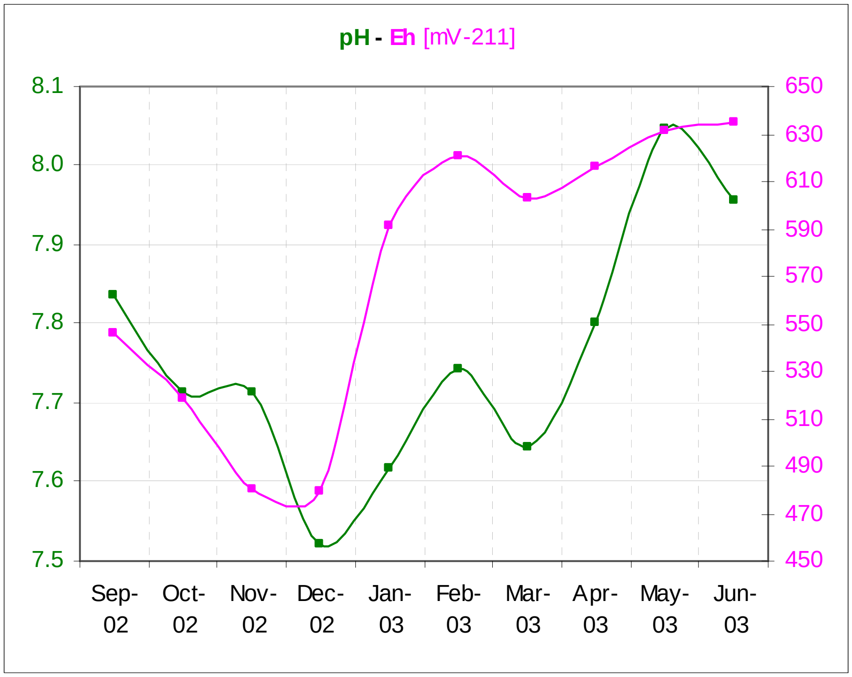

Figure 45. Relation between pH and Eh in the Wonderfonteinspruit, based on monthly-average values

Both time series show a distinct drop to low values during early summer (Nov–Dec) and a steep rise to significantly higher levels for the remaining part of the time. Interestingly a drop in March interrupts the otherwise continuous increase of both parameters (Figure 45).

This similar behaviour suggests a direct proportional relation between the two parameters. This, however, is contradicted by their inverse physical relationship, where increasing pH values correspond with decreasing Eh values (Winde, 2002).

This again points to additional factors superimposing the pH–Eh relationship in the Wonderfonteinspruit. Again this is supposedly related to the influx of high volumes of acidic rainwater into the stream that lowers pH. The simultaneous drop of Eh is unexpected since rainwater generally displays an elevated redox potential. However, with much of the rainwater recharging the dolomitic groundwater instead of entering the stream directly, this might result in significantly lower Eh values. With rising groundwater volumes entering underground mine workings, higher discharge rates result that may lower the Eh in the Wonderfonteinspruit.

pH–EC relation

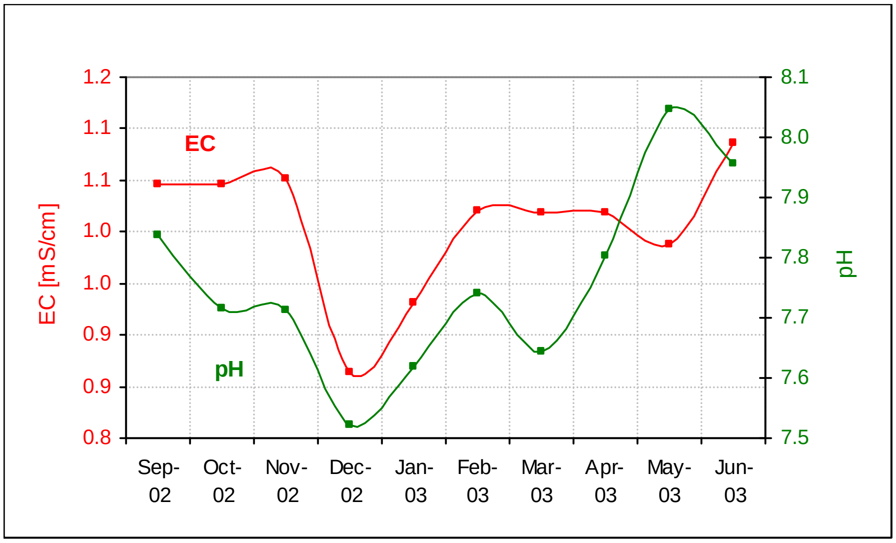

Figure 46. Relation between pH and Eh in the Wonderfonteinspruit at C2H069, based on monthly-average values

According to Figure 46 the relation between EC and pH changes during the measurement period. While the first eight months display homodirectional changes of both parameters indicating a direct proportional relationship, the last two months (May and June 2003) show an inverse behaviour where the EC drops while the pH rises. Occurring in the non-raining period, with no possible dilution by rainfall, the dropping EC might indicate either:

a) a decrease in waste-water discharges or

b) an increase in discharges of less-contaminated fissure water.

The latter is supported by the associated rise of the pH indicating higher volumes of dolomitic (and therefore alkaline groundwater). Possible reasons for this on which one can only speculate, having no additional information, might include technical problems of using fissure water for other internal purposes or the interception of a water-bearing cavity during underground operations.

While the relationship of the monthly-average values seems to change during the measurement period, the temporal dynamics of both parameters in terms of their maximal monthly fluctuation are similar and constant throughout the observation period (Figure 47).

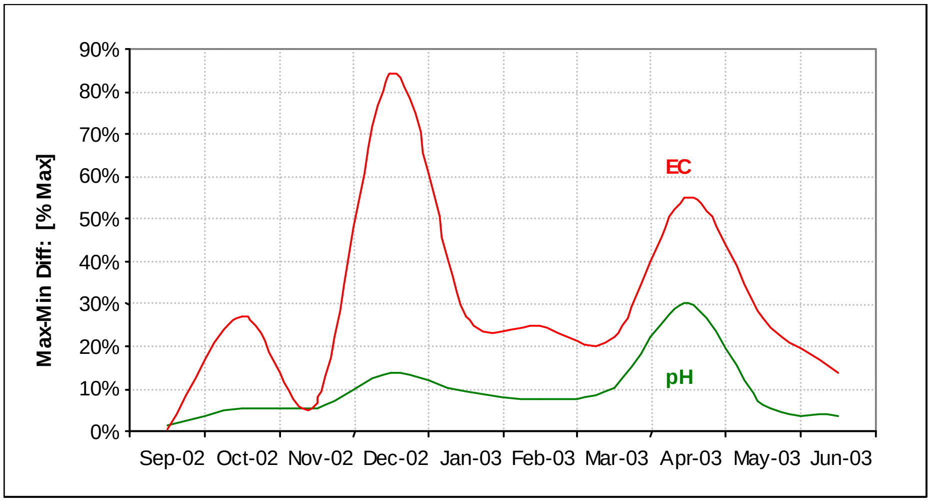

Figure 47. Relation between maximal monthly fluctuations of pH and Eh in the Wonderfonteinspruit at C2H069

Eh–EC relation

The long-term behaviour of the monthly averages of EC and Eh seems to be rather similar, both showing a significant drop in December 2002 with a subsequent steep increase (Figure 48).

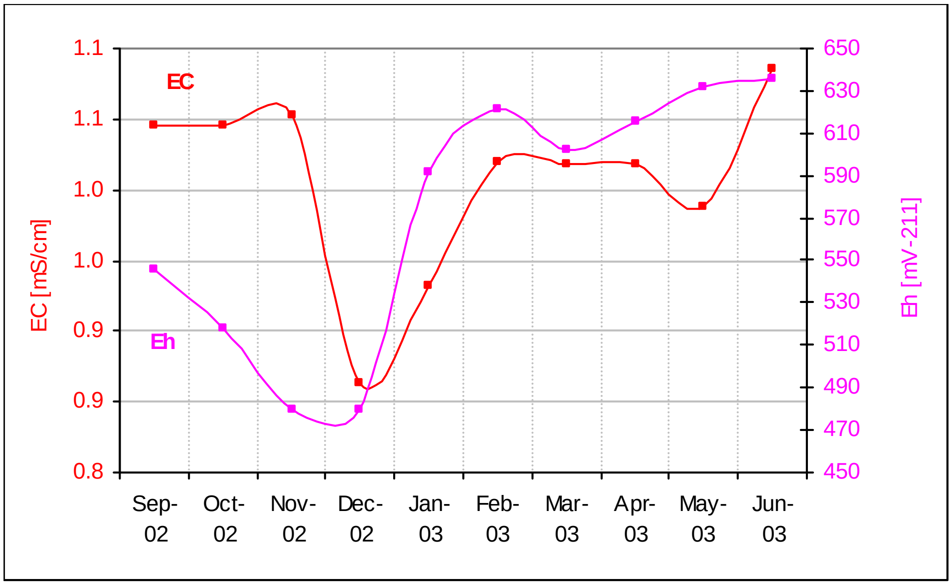

Figure 48. Time series of EC and Eh in stream water of the Wonderfonteinspruit, based on monthly averages, displaying a certain similarity regarding their temporal dynamic over the measurement period (Sep 2002–Jun 2003)

As suggested earlier, this might be caused mainly by the influx of rainwater. Similar to the relation between pH and Eh, the relation between Eh and EC seems also to change from a direct into an inverse one during the last two months, where the decrease of EC coincides with an increases of Eh (May 2003) and vice versa (June 2003). This also supports the assumption based on the Eh–pH relationship that the hydrochemical regime somehow changed during these months. Having no data on previous winter months, this change might reflect a seasonal rather than an anthropogenic or technological effect.

8.4.2 Relationships between parameters based on time series of real-time measurement

In contrast to monthly-average-based time series, which are affected by short-term events such as rainstorms increasing or lowering the monthly mean significantly, time series based on 5- or 10-min. measurements are free of such statistical effects that often mask the actual relation between parameters. For this reason the following explores the relation of parameters based on real-time measurements.

Water temperature and pH

Figure 59 illustrates that both parameters show similar diurnal oscillations, most clearly indicated by their coinciding daily maxima.

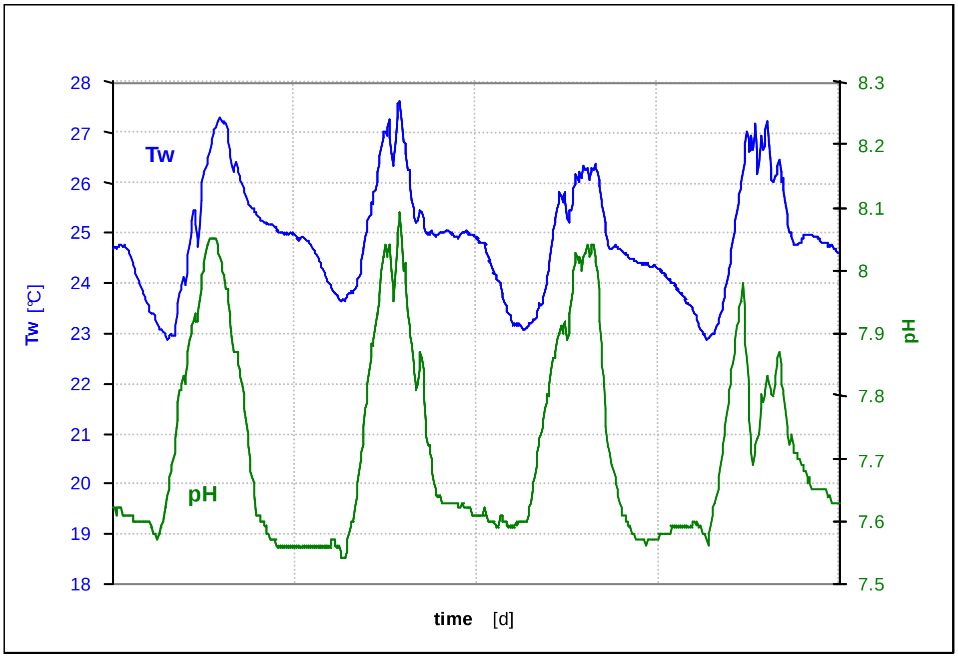

Figure 49. Ten-minute-interval measurements of water temperature and pH in stream water of the Wonderfonteinspruit displaying a degree of similarity regarding their diurnal fluctuations during a typical four-day period (1–4 February 2003)

While displaying almost identical diurnal rhythms, the real-time-based charts for both parameters contradict the finding derived from monthly-average analyses that suggested an inverse relationship. With both, the temperature, as well as the pH-cycle, being driven by daily changes of solar-radiation intensity, a direct relationship is, however, also the more plausible one. Apart from their common dependence on the radiation input, this relationship is strengthened by the fact that rising temperatures reduce the solubility of CO_2, which in turn leads to higher pH-values.

Water temperature and redox potential

The real-time measurements for both parameters are shown in Figure 50.

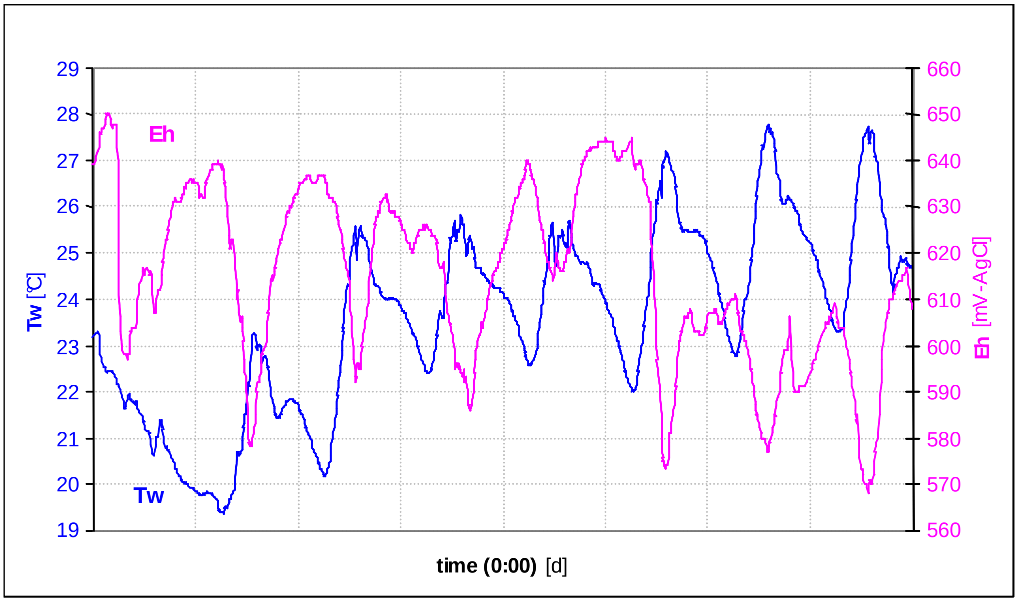

Figure 50. Ten-minute-interval measurements of water temperature and Eh in stream water of the Wonderfonteinspruit displaying a degree of similarity regarding their diurnal fluctuations during a typical eight-day period in January 2003 (24–31)

Figure 60 clearly indicates that Eh fluctuates inversely to the water temperature, i.e. reaching its daily maximum during the night and decreasing to a minimum value occurring late afternoon, since rising water temperature lowers the concentration of dissolved O_2, which — as a major electron donator — may in turn lower the redox-potential. It was, however, found that the influence of the oxygen concentration in water on the redox-potential is far weaker than that of pH changes (Winde, 2003). It is therefore more likely that the Eh dynamic is only dependent on water temperature as far as the latter has an impact on the pH that, in turn, largely controls the redox potential.

pH and Eh

Real-time measurements illustrating a typical period of diurnal fluctuations for both parameters are shown in Figure 61.

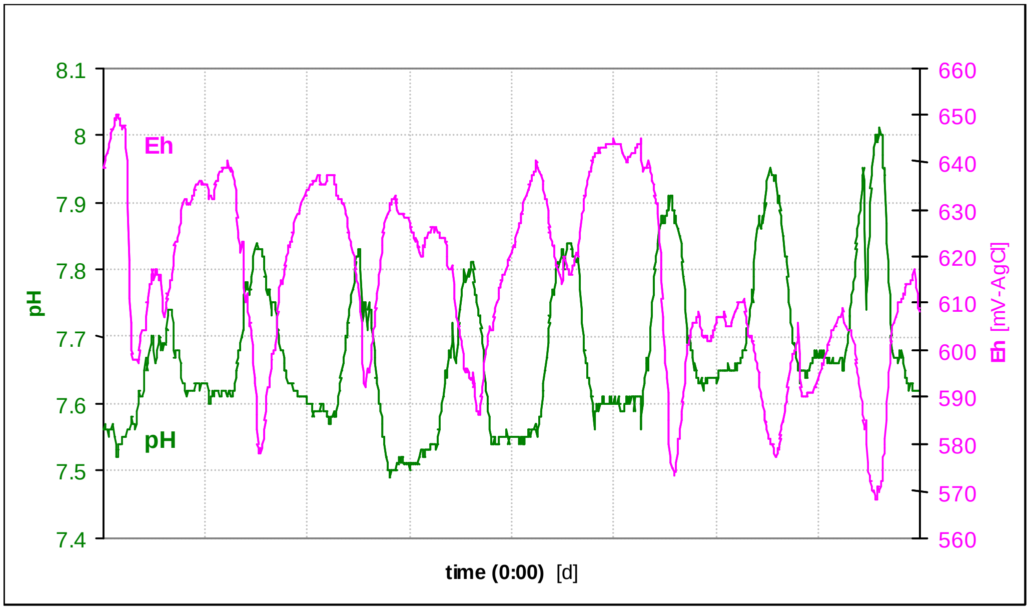

Figure 51. Ten-minute-interval measurements of pH and Eh in stream water of the Wonderfonteinspruit displaying an inverse relationship of their diurnal fluctuations during a typical eight-day period in January 2003

The relation of the pH to Eh behaves similarly to the relation between pH and water temperature, changing from what is thought to be a direct proportional one (based on monthly-means analyses) to an inverse (indirect proportional) relationship in real-time-based charts. While the monthly-average chart suggests a similar behaviour for both parameters (Figure 45), the time series based on 10-min. intervals shows that both parameters fluctuate inversely to each other.

8.5 Response of parameters to events (F. Winde)

In addition to re-occurring oscillations, the response parameters to events such as rainstorms or discharges of waste water were also analysed by using examples of selected events observed during the measurement period. However, the interpretation of event-related changes of hydrochemical parameters in the Wonderfonteinspruit is complicated by the fact that no accompanying meteorological or flow data are available. In the absence of the latter, the interpretation of charts is based on the following assumptions:

- Rain water generally displays a significantly lower EC (distillation effect) and pH (acid rain) than the Wonderfonteinspruit as receiving stream

- Seepage from slimes dams shows significantly higher EC (mainly owing to dissolved sulphates) and lower pH (formation of sulphuric acid due to pyrite oxidation) than stream

- Waste water from industrial, mining or municipal sources often displays an elevated EC and pH compared with water in the receiving stream.

- Parameter changes caused by anthropogenic discharges are likely to display graphs distinctly different from those caused by natural processes. Switching waste-water pumps on and off frequently results in square-like hydrographs with almost vertical limbs indicating constant intensity. This is unlike natural processes, which are characterised by changing intensities (usually decreasing in the process) resulting in ‘softer’ hydrographs.

8.5.1 Event on 28/12/2002

The direction and gradient of changes of pH, EC and Tw occurring on 28 December 2003 point to a rainstorm as triggering event (Figure 52).

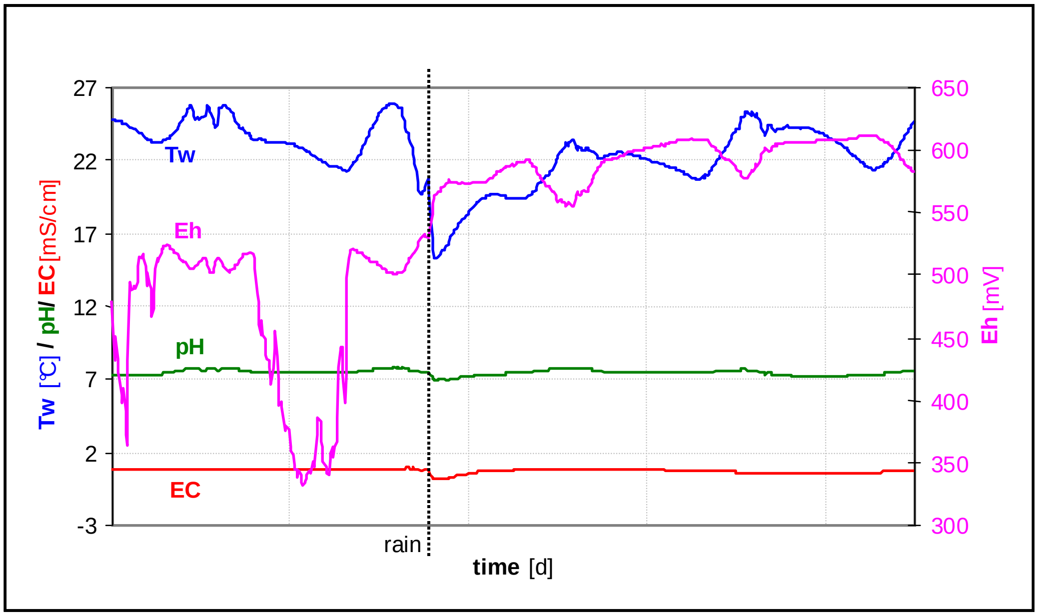

Figure 52. Gradient and direction of changes of pH, Tw, Eh and EC in the Wonderfonteinspruit on 27 Dec. 2003 pointing to a rainstorm as a possible cause

Apart from decreasing pH and EC, a drop in temperature and increasing Eh are also observed (Figure 52).

That suggests that the rainwater is cooler and more oxidising than the stream water in the Wonderfonteinspruit. While the redox potential of rainwater is likely to remain higher than the stream water throughout the seasons, the relation of rain temperature to stream temperature might vary, depending on the seasons.

8.5.2 Event series in January 2003

A series of significant and sudden drops of the EC during January 2003 point to a succession of rain events affecting the Wonderfonteinspruit (Figure 53).

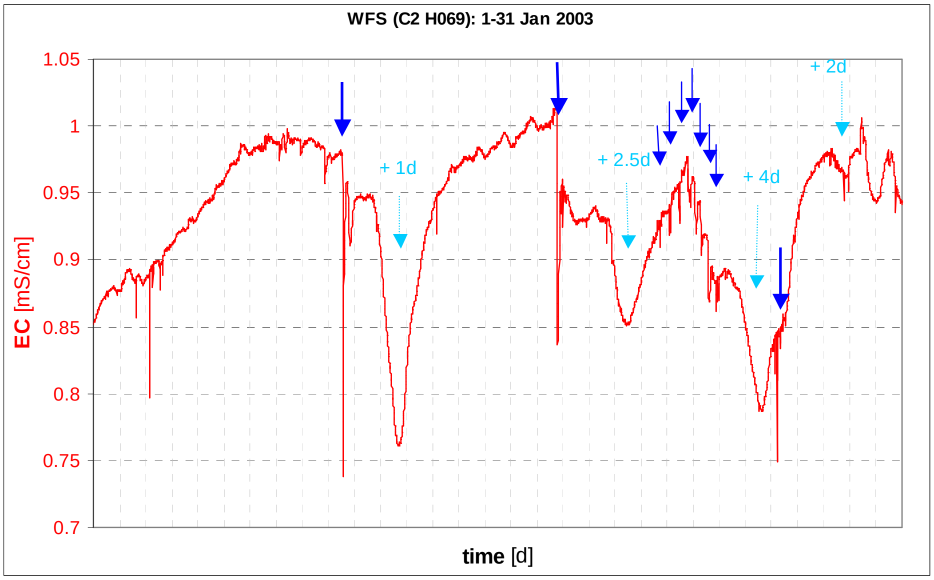

Figure 53. Sudden and pronounced drops of the EC during January 2003 point to a series of successive rainstorms (time of supposed occurrence is indicated by solid-line arrows) affecting the Wonderfonteinspruit. Each event is followed by a less-steep, but longer-lasting, drop of the EC occurring one to four days after the first EC drop of each event (indicated by dashed arrows)

It is interesting to note that each sudden drop of the EC is followed by a second longer-lasting drop that occurs one to four days after the initial one (Figure 53). It seems that the time lag between the first and the second EC drop is the shorter the more pronounced the first EC drop is. The latter, in turn, is likely to reflect the intensity of the rain event. The assumption that these changes are triggered by rainstorms is further supported by simultaneous drops of the pH, indicating the inflow of acidic rainwater[11], and by suppressed diurnal pH oscillations (Figure 54).

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[11] Measurements of the pH in rainwater, undertaken in 1999–2000 in Potchefstroom, yielded pH values as low as 3,7 (Winde, 2003).

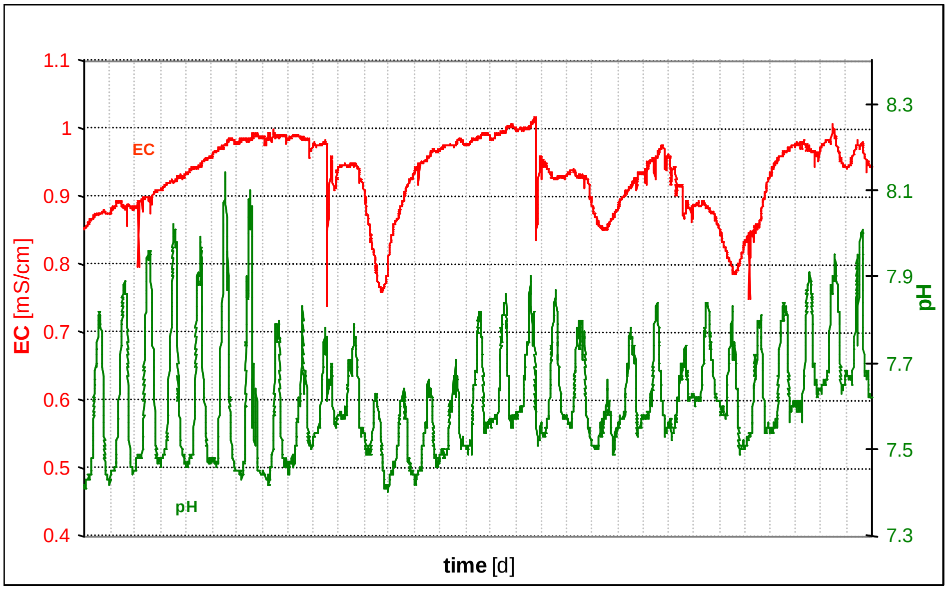

Figure 54. Pronounced diurnal oscillations of the pH are markedly reduced during rain events, indicated by sudden drops of the EC (1–31 January 2003)

Regarding the observed dynamic of the EC the question arises as to the cause of the second longer-lasting drop of the EC following each rain event.

An analysis based on a higher temporal resolution of a comparable rain event in December (28/12/2003) reveals that the response of EC to a rain event can be subdivided into three phases (Figure 55).

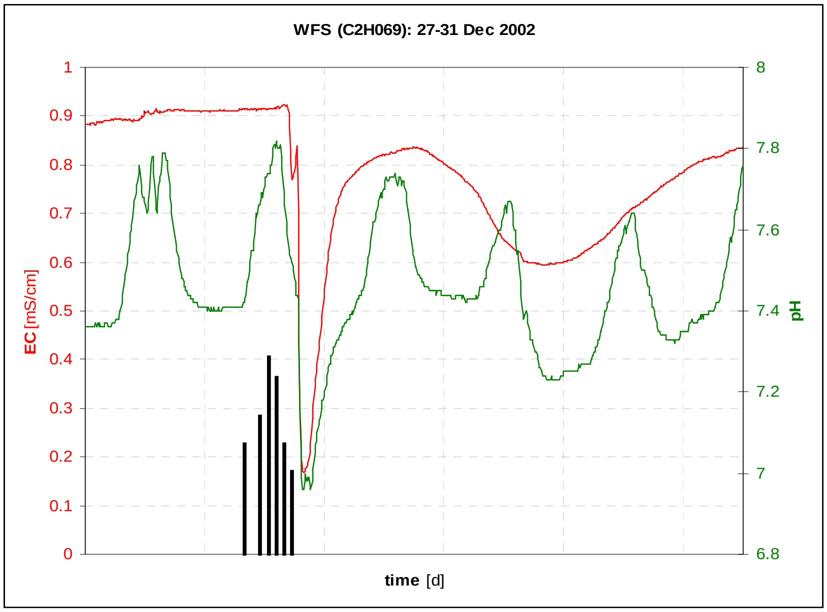

Figure 55. pH (lower line) and EC (upper line) during a rain event on 28 December 2002 showing a ‘bouncing back’ response of the EC (27–31 December 2002)

The *first phase* occurs almost immediately after the beginning of the rain event, featuring a sudden sharp drop of the EC to about 20 per cent of the pre-event level within less than an hour. Accompanied by simultaneous drops of the pH, this points to rainwater and quick surface run-off entering the stream directly.

After reaching the minimum, the *second phase* sets in during which the EC recovers to almost pre-event levels within a few hours. With gradually decreasing intensity the EC reaches a plateau on which it remains for one to four days. This reflects decreasing volumes of low EC rainwater run-off flowing into the stream and rising proportions of (polluted) stream water. The fact that the level of the plateau is slightly below the pre-event level reflects the dilution of stream water with rain in the upper parts of the catchment.

In *phase 3* the EC drops again to almost the same level as that of the initial drop. Lasting for one to three days, the second drop is significantly less sharp compared with the initial one, suggesting a less-intense inflow of low-EC water. This suggests that rainwater is again entering the stream. A significantly lower steepness of this EC drop suggests that the rainwater does not originate from a (possible) second rain event, but flows into the stream via a different mechanism of lower intensity. Occurring always with a delay of one to four days after an initial rain event, it is very likely that the second EC drop is caused by rainwater from the first event whose inflow into the stream was somehow delayed. The following processes might cause this delay:

a) Increased discharge of relatively clean fissure water from underground consisting of rainwater ingressing at increased rates into the mine void after rain events.

With more than 1 km of dolomite overlying the mine void, the time rainwater needs to percolate through would explain the observed delay between the rain event and the EC drop of several days. Percolating through overlying strata in close contact with dolomitic rock, an increase of the pH of the rainwater is to be expected. Compared with phase 1, the pH in phase 3 is elevated and would confirm this (Fig. 52).

It was, however, also observed that the second EC drop follows a preceding rain event more quickly the more intense this event was. In view of the rather low hydraulic permeability of most of the rock strata between the weathered zone of the upper dolomite and the mine void, higher rainfall intensity must not necessarily result in higher infiltration rates that could explain such a relation.

The fact that the shape of the EC graphs is not ‘square like’, despite being of anthropogenic origin, might be attributed to flow retention in relatively large wetlands upstream of station C2H069.

b) Discharge of rainwater run-off collected in stormwater-drainage systems including stormwater-retention dams.

With most stormwater-drainage systems having only very limited retention capacity, this would explain the relation between rain intensity and time lag of the EC response. It is, however, unlikely that the delay between rain event and discharge of the resulting stormwater run-off is in the order of several days.

c) Overflowing rainwater from near-surface karst cavities.

With many sinkholes providing conduits for accelerated groundwater recharge, rainwater may fill near-surface dolomitic cavities. Where such cavities are isolated and not connected to large underground caves or mine workings, they might be filled with infiltrating rainwater until they overflow, releasing rainwater back into the stream. Depending on the volume of such cavities (capacity to store water), this would result in a certain delay and also explain the relation between rain intensity and time lag of the EC response.

The time spans for each phase are illustrated in Figure 56, displaying an event on 9 Jan. 2003.

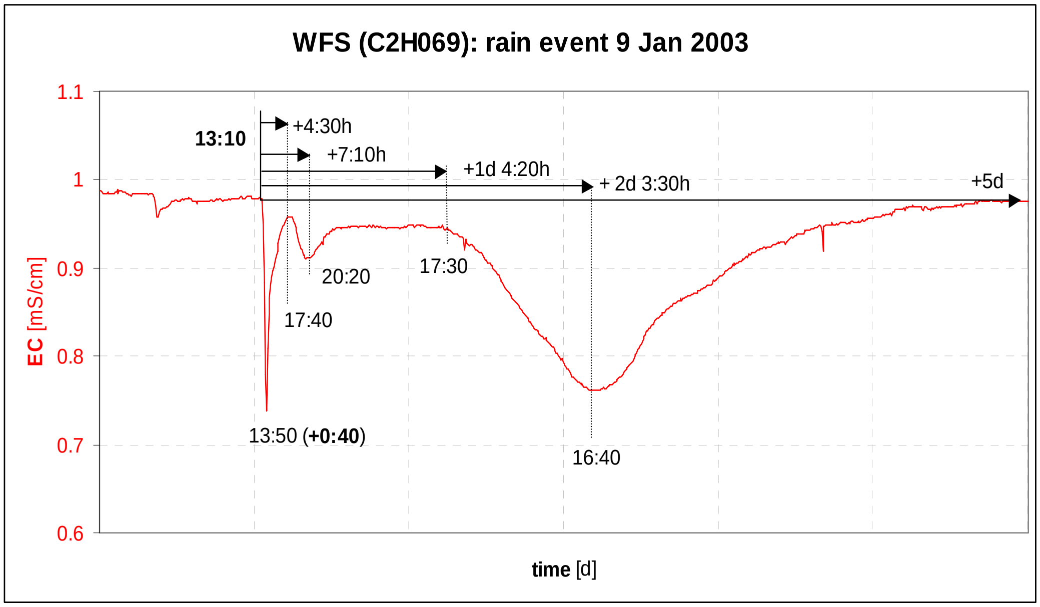

Figure 56. Temporal dynamic of a typical EC response to a rain event on 9 Jan. 2003

In addition to the three phases discussed, an additional small drop of EC occurs shortly after the initial one, supposedly caused by a second less-intense rain event.

8.5.3 *Events of 11/5/2003*

Two events of a different nature were observed on 11 May 2003 when sudden drops of the EC indicated the inflow of clean water (Figure 57).

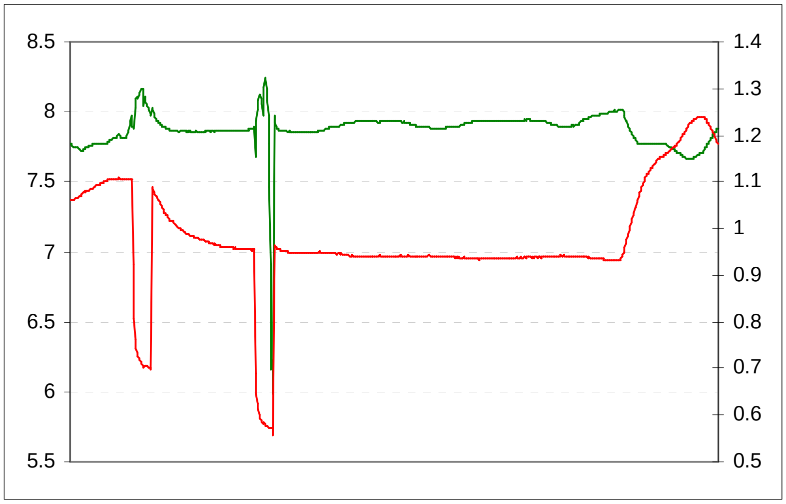

Figure 57. Responses of the pH (upper line, left y-axis) and EC (lower line, units on right y-axis) to two events on 11 May 2003

Being accompanied by rising pH values indicates that this could not have been caused by rainwater which, in general, has a lower pH than the stream. Since the shape of the EC drop is typical for opening and closing pipes rather than natural flow processes, this points to anthropogenic causes of the two events. Furthermore, the pH during the second event drops significantly after having risen moderately. The pH increase and subsequent plunging during one single event makes anthropogenic causes of a technical nature even more a likely cause.

8.6 Conclusions and recommendations (F. Winde)

The mobility of dissolved metals is largely controlled by pH and Eh. For both parameters distinct diurnal and seasonal fluctuations were found, superimposed by event-related variations. Such fluctuations 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 co-precipitation.

While the pH threshold for the precipitation of Fe-hydroxide (>7) is generally exceeded throughout the year, presumably owing to the influence of dolomite, daily increases 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 aids lower uranium concentrations. 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 uranium concentrations in 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 (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 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 parameter 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 can be observed in real-time measurements.

The EC of the Wonderfonteinspruit appears to be rather constant on a 1 mS/ cm level, elevated above background by some 0,5–0,7 mS/cm. The EC is dominated by SO_4 originating from mine effluents (oxidised sulphides such as pyrite found in the mined ore). In contrast to pH, Eh and water temperature, the EC shows no diurnal oscillations and no consistent seasonal oscillations (e.g. increase during low-flow dry season and decrease during high-flow wet season). It reflects, however, events such as rainstorms or waste-water discharges by pronounced short-term fluctuations.

Using the relation between EC and pH, the nature of events can be analysed. This includes the influx of rainwater after storm events (indicated by simultaneous drops of pH and EC) and the influx of seepage indicated by an inverse behaviour of (dropping) pH and (increasing) EC. However, it is important to use real-time data instead of mean values in order to prevent wrong conclusions.

The extent and temporal dynamic of event-related EC changes may also assist to understand and predict responses of the fluvial system to certain events. This may include the calculation of groundwater-recharge rates and the quantification of surface run-off coefficients. The latter may assist in estimating stream flow during the initial (‘dry’) phase of rewatering.

Sudden pulses of uranium released from solid-sediment phases owing to changing hydrochemical conditions after rain events and discharge of waste water seem to be unlikely. It was, however, found in other streams that highly contaminated porewater was hydraulically displaced by infiltrating groundwater, resulting in a short-term increase of the concentration of dissolved uranium in stream water immediately after a rain event. Such mechanisms were not investigated at the Wonderfonteinspruit, but may occur there as well.

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 for a 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 in high temporal resolution.

9 Risk assessment (P. Wade, F. Winde and H Coetzee)

9.1 *Summary*

9.1.1 Chemicals of potential concern

Uranium was chosen as the chemical of potential concern, based on the results presented in Section 4.3 (Identification of contaminants of concern).

9.1.2 Exposure assessment

Uranium can enter the human body via a number of pathways from the source, which is 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.

9.1.3 Toxicity assessment

The primary organ at risk from uranium chemical toxicity is the kidney. Other organs at risk from chronic radiological toxicity include the lymph nodes and the bone. A recent review of uranium toxicity by WISE (2003) set Minimum Derived Drinking Water Concentrations at 31 µg/l for chemical toxicity, and 63 µg/l based on 1 mSv/a, 500 l/a radiological risk. It should be noted that there is practically no lower limit for acceptable radiological risk, based on a linear dose-response profile.

9.1.4 Risk characterisation

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, which means that there is a risk of ill-health effects by drinking water from contaminated streams in the Wonderfonteinspruit catchment.

Studies of the Wonderfonteinspruit catchment (Kempster *et al.*, 1996, IWQS, 1999) 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.

9.2 *Introduction*

9.2.1 Overview (General problem at site)

Studies by the Department of Water Affairs and Forestry have indicated elevated levels of radioactivity in rivers draining the gold-mining areas of the Witwatersrand. A detailed study of the Mooi River system (including the Wonderfonteinspruit) showed radioactivity levels in this system to be elevated, although doses to the public from formal drinking water sources were found to be within acceptable limits at most sites.

Following this study, Wade et al. (2002) showed that the river sediments act as a sink, holding radionuclides, often at concentrations considerably higher than those found in the sources (gold/uranium ores and mine tailings). Wade has further demonstrated that the uranium in these sediments may be mobilised by changes in water chemistry. Coetzee and Chevrel (2000), using airborne gamma-ray spectrometry, showed that the radioactivity in the sediments has a similar Bi-214/Tl-208 ratio to the mine tailings within the catchment. This technique does not, however, have the necessary sensitivity to relate individual polluted areas to specific sources. Furthermore, the volume and degree of contamination, and the composition of the contaminants in these sediment bodies, are unknown.

Frank Winde collected continuous monitoring data, covering a number of physicochemical parameters measured at 10-min. intervals over a period of one and a half years in the Koekemoerspruit near Klerksdorp and two years in the Wismut area (Germany). These data show that significant variations in the chemical conditions of the river water can occur over periods of hours or less, suggesting that existing data on samples collected at a much lower frequency, particularly those collected in a regular weekly schedule, may not adequately represent the short-term variations in chemistry. Data from the Wismut sites in the former East Germany show even more pronounced short-term variations in chemistry than the Koekemoerspruit (Winde, 2001; Winde and De Villiers, 2001; Winde, 2003; and Winde et. al., 2004a/b).

Eglington and coworkers have demonstrated that the contributions of different sources to polluted ground and river water can be quantified using isotopic analyses. This approach can also be extended to include the material bound to the sediments, and can give an estimate of the contributions of different mining areas and potentially different mines to the pollution load within the river system. This information is required in order to establish priorities for remediation and further study within the catchment (Eglington et al., 2001).

The current project was motivated and conceived as a direct result of the Department of Water Affairs and Forestry’s study of radioactivity in the Mooi River Catchment (IWQS, 1999), and a follow-up study undertaken by Wade et al. (2002). During this period, considerable scientific debate occurred regarding this subject and the correct approach to the issues at hand. This study aimed at replying to a number of the questions that were raised in that debate, as well as extending the understanding of sediment-water interactions within the catchment to include non-radioactive metals. During the course of the study, an additional more-focused study was undertaken of an individual farm dam (Coetzee et al., 2003). The results of the latter study have, in part, led to somewhat controversial legal proceedings being launched by the Potchefstroom City Council against one of the mining companies perceived as being a significant polluter, the Department of Water Affairs and Forestry, and the farmer on whose farm the dam is situated.

Owing to the often emotionally charged nature of problems regarding uranium and the limitations in the budget of this project, which precluded regular sampling and analysis, those portions of the risk assessment that look at the pathway due to ingestion of water use uranium concentration data collected for the DWAF study of radioactivity in the Mooi River catchment (IWQS, 1999). These data represent a regular year-long sampling programme, with analyses performed by an NNR recognised laboratory.

9.2.2 Site-specific objectives of the risk assessment

Because of the heated 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 was that of a risk assessment, as implemented by the US EPA.

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 authority 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. A baseline risk assessment should incorporate some or all of the following:

- Description of the history of pollution in the system and the pollution sources.
- Description of the mechanisms and pathways of contamination.
- Presentation of measurements of the range of physicochemical parameters currently encountered in the river system which could influence these pathways, as well as estimates of the likely extrema.
- Presentation of estimates of the volumes of contamination in the Wonderfonteinspruit system, the degree and nature of immobilisation of the contamination, and the likelihood of remobilisation of the contaminants.
- Presentation of all results in terms of risk to the communities in the catchment, as well as downstream, particularly in Potchefstroom.

9.2.3 Overview of study design

Risk-assessment method applied

The USEPA Risk Assessment Guidance for Superfund (RAGS) Process (USEPA, 1997a) for baseline risk assessments was used in this investigation. The methodology used here is similar to that published by Servant (2002) “Methodology to assess the radiological impact of a repository for uranium mill tailings after remediation (short-term impact)”.

The stages of Servant's (2002) radiological- and chemical-impact assessment of uranium are as follows:

- Description of the local environment
  - Local meteorological conditions
  - Geology ─ hydrogeology
  - Hydrographical system
  - Agricultural environment

    - Water uses
    - Description of the human environment

- Site description
    - Description of the wastes
    - Repository structures
    - Water management
    - Workings

- Conceptual model

- Exposure pathways
    - External exposure
    - Internal exposure via inhalation
    - Internal exposure via ingestion

- Development of population groups and scenarios
    - Location of population groups
    - Composition of population groups
    - Scenario definition

- Measurements in the environment
    - Water
    - Food chain

- Initial radiological level

- Site-impact calculation
    - Dose coefficients
    - Sensitivity analysis ─ uncertainty
    - Comparison with regulatory limits

Rationale for using the United States Environmental Protection Agency (USEPA) Risk Assessment Guidance for Superfund (RAGS) Process

Because of the sensitive nature of the information to be generated in this study, it was felt necessary to use a tried-and-tested methodology that has been "bomb-proofed" by application in a variety of controversial environmental and social environments. The USEPA Superfund processes fit these requirements exactly (USEPA, 1997a).

The Risk Assessment Guidance for Superfund manuals used in this study was developed to be used in the remedial investigation/feasibility study (RI/FS) process at Superfund sites, although the analytical framework and specific methods described in the manuals may also be applicable to other assessments of hazardous wastes and hazardous materials.

Although human health-risk assessment and environmental assessment are different processes, they share certain common information requirements and generally can use some of the same chemical sampling and environmental-setting data for a site. Planning for both assessments should begin during the scoping stage of the RI/FS, and site sampling and other data-collection activities to support the two assessments should be coordinated. Use of the USEPA manuals facilitates this coordination.

Overview of the RAGS rocess Applicable to the Baseline Risk Assessment

The process investigated as applicable to a baseline risk assessment in the Wonderfonteinspruit catchment is graphically presented in Figure 58.

The Planning Tools developed by the EPA RAGS Part D Workgroup, and refined through regional review, include a Technical Approach for Risk Assessment or TARA, Planning Tables, and Instructions for the Planning Tables.

The Technical Approach for Risk Assessment (TARA) is a road map for incorporating continuous involvement of the EPA risk assessor throughout the CERCLA remedial process for a particular site. Risk-related activities, beginning with scoping and problem formulation, extending through collection and analysis of risk-related data, and supporting risk-management decision making and remedial-design/remedial-action issues are addressed.

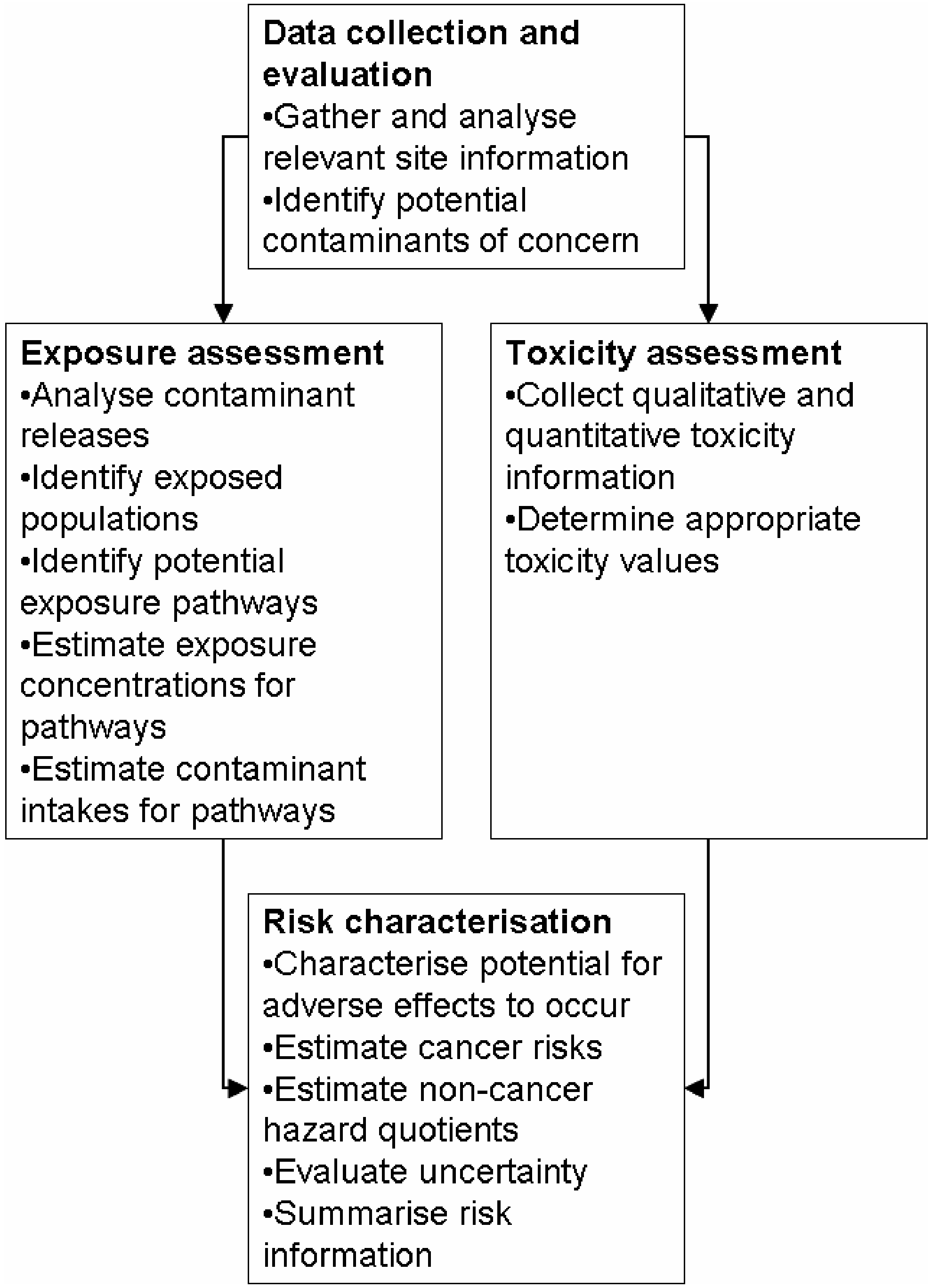

Figure 58. Schematic overview of the RAGS Part A Baseline Risk Assessment (USEPA, 1989a)

The use of EPA planning tools

The guidance documents presented by the TARA in the four CERCLA remedial process phases are: During scoping, During the remedial investigation, During the feasibility study, and After the feasibility study. It is recommended that the elements identified in the TARA be customised for each site-specific human health-risk assessment, as appropriate. These elements should be included in project workplans to better define that risk assessment, and to facilitate more standardised planning.

The Planning Tables have been developed to document more clearly and consistently important parameters, data, calculations and conclusions from all stages of human health-risk assessment development.

For site-specific risk assessments, the Planning Tables, related Worksheets and Supporting Information should first be prepared as Interim Deliverables for review, and should later be included in the Draft and Final Baseline Risk Assessment Reports.

Use of the Planning Tables helps to standardise the reporting of human health- risk assessments and to improve communication with stakeholders.

Instructions for the Planning Tables have been prepared corresponding to each row and column on each Planning Table. Definitions of each field are supplied in the Glossary and example data or selections for individual data fields are provided. The Instructions should be used to complete and/or review Planning Tables for each site-specific human health-risk assessment, where appropriate.

Methodological considerations

This study has been undertaken as follows:

Phase	Activities
Phase 1 — Reconnaissance	Semiquantitative scans were used to identify contaminated sites, as well as the contaminants of greatest concern. These data were used to focus a quantitative risk assessment.
Phase 2 — Risk assessment	Quantitative analyses were carried out with the aim of quantifying the risk to impacted populations and environments, and identifying the uncertainties in this risk assessment.

A formal risk-assessment methodology was applied to the catchment, using the results obtained, and the potential risk was determined.

9.2.4 Site background

Background information regarding the site is contained in the preceding chapters.

9.2.5 Site identification

The site identification is presented in RAGS Table 0 (Table 10).

Table 10: RAGS Table 0: Site Risk-Assessment Identification Information

TABLE 0	
SITE RISK-ASSESSMENT IDENTIFICATION INFORMATION	
Wonderfonteinspruit catchment	
Site Name/OU:	Wonderfonteinspruit catchment
State:	Gauteng and North West Provinces
Status:	
National facility (Y/N):	
Project Manager:	Henk Coetzee
Risk Assessors:	Peter Wade, Frank Winde
Prepared by (organisation):	Council for Geoscience
Prepared for (organisation):	Water Research Commission
Document title:	A methodology for the assessment of current and future water-pollution risk with application to the Mooirivierloop (Wonderfonteinspruit)
Document date:	1 October 2003
Probabilistic risk assessment (Y/N):	N

9.2.6 Site description

The site has been described in Section 1.1 of this report.

Description of the local environment

Water management

Water-management aspects of the Wonderfonteinspruit have been presented in Section 2.6 of this report.

9.2.7 Map of site

Maps of the region of interest are presented as Figure 1 and Figure 2.

9.2.8 General history

Ownership and operations

General history of the site is discussed in Section 1.3.1 of this report.

Contamination

Contamination issues are described fully in Section 2 of this report.

9.2.9 Historical studies of the site

CGS radiometric studies

During 1991 the Council for Geoscience undertook high-resolution airborne radiometric surveys of large parts of the Witwatersrand. The high-resolution data showed that not only did mine-waste deposits emit significantly more gamma radiation than the surrounding environment, but that the wetlands downstream of the mining areas were also contaminated. In addition to the radionuclides, other metallic contaminants have been located in the radioactively anomalous areas (Coetzee and Szczesniak, 1993).

Study by DWAF

During 1997, an intensive sampling programme was undertaken in the Wonderfonteinspruit catchment. It was found that mining activities in the area are a major contributor to the radionuclide content of the water, specifically with respect to uranium and uranium-series nuclides, and that the activities of dissolved radionuclides decreased downstream of mining activities (IWQS, 1999).

Study by the CSIR

Following this finding, Wade et al. (2002) undertook a study funded by the Water Research Commission to investigate the fate and transport of selected radionuclides within the catchment. Radionuclides were found to be concentrated in the wetland sediments throughout the catchment, and the processes concentrating the radionuclides were found to be reversible, potentially remobilising radionuclides, and leading to contamination of downstream water resources.

Studies by the CGS

This potential for downstream contamination was identified as a specific concern for the water supply of the City of Potchefstroom (Coetzee et al., 2003). The Council for Geoscience was commissioned to undertake a study, which had three major conclusions:

1. The study confirmed the results for uranium of Wade et al. (2002), with uranium concentrations of several hundred mg/kg being found in the sediment (the expected natural background concentration for a dolomitic area such as this would be less than 1 mg/kg).

2. The study also identified a number of other heavy metals of concern, and noted that these appeared to follow the same behaviour as the radionuclides described by Wade et al. (2002).

3. Based on laboratory studies and chemical modelling, the metals (uranium-series radionuclides are all metals, and behave chemically as such in the environment) are adsorbed or chemisorbed to a number of sediment phases, all of which can be rereleased by plausible geochemical processes.

These two studies on sediment concluded that, while current conditions are relatively stable, albeit not totally effective at removing metals from the water, the unpredictability of the future requires management plans that will either maintain conditions as they are ad infinitum, or will have to contemplate rehabilitation of the contaminated areas within the environment.

Following the production of the second report on sediments, the dam in question was drained, exposing the sediments to an oxidising environment, one of the re-release scenarios described in the report. At this point, the Potchefstroom City Council took legal action against one of the gold mines responsible for the contamination. This case was settled out of court, with the mine agreeing to rebuild the dam wall and rehabilitate the environment.

9.2.10 Significant site reference points

Significant site reference points are presented in Section 4 of this document.

Scope of the risk assessment

Knowledge of the scope of the assessment is critical (USEPA, 1992). Scope can be understood as “comprehensiveness”, for example, where exposure to multiple chemicals, perhaps considering only certain significant chemicals, may yield the same risk estimates as a very detailed analysis.

Knowledge of the purpose of the risk assessment usually helps define the scope.

Risk assessments usually follow a tiered approach, in which the scope of the assessment is narrowed upon successive iterations. In the first tier of the risk assessments, measurements are taken in the region of interest, and compared with a standard, e.g. IWQS study, and Wade et al. (2002).

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 (USEPA, 1992).

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.

9.2.11 Organisation of a risk assessment report

The report structure is as suggested in Exhibit 9-1 of USEPA (1989a) “Risk Assessment Guidance for Superfund ─ Volume I: Human Health Evaluation Manual (Part A)”.

9.3 Preliminary conceptual analysis

9.3.1 Process issues

While the US Environmental Protection Agency presents the Development of Conceptual Model, the Identification of Chemicals of Potential Concern and the Identification of Exposure Pathways phases as separate issues, in practice there is much “jumping” between the phases, as one successively refines one's hypotheses, based on information gathered in a “tiered” fashion.

When the final report is compiled, it is useful to present the information in the above separate headings. Some unavoidable confusion may result from the fact that information gathered in a single exercise must be presented in a linear order. For example, information presented in the above process diagram was derived in the same brainstorming exercise that yielded the identification of exposure pathways and determination of chemicals of potential concern.

9.3.2 Conceptual model

A conceptual model of the site (in this case the Wonderfonteinspruit catchment) was developed for this study. This is a critical component of the risk assessment, as it forces the

Risk Assessors and the Interested and Affected Parties (I and APs) to agree at an early stage in the investigation on the problem parameters.

Benefits of developing a conceptual site model include the following (USEPA, 1998)

- The process of creating a conceptual model is a powerful learning tool.
- Conceptual models are easily modified as knowledge increases.
- Conceptual models highlight what is known and not known, and can be used to plan future work.
- Conceptual modelling can be a powerful communication tool, providing an explicit expression of the assumptions and understanding of a system for others to evaluate.
- Conceptual models provide a framework for prediction and are the template for generating more risk hypotheses.

Development of the conceptual model is facilitated by working through a checklist on the template in Figure 59. This checklist acts as a thinking aid to developing a complete picture. If the conceptual model is developed in a large gathering of project personnel and I and APs, facilitation of this development process using Systems Thinking and Strategic Assumption Surfacing Techniques is advised.

Conceptual models consist of two principal components (USEPA, 1998):

- A set of risk hypotheses that describe predicted relationships among stressor, exposure, and assessment end-point response, along with the rationale for their selection.
- A diagram that illustrates the relationships presented in the risk hypotheses.

The optimal process of developing a conceptual model includes a list of variables and hypotheses to be tested, organised into categories of Sources, Pathways and Receptors (Figure 59, USEPA, 1989a).

The next step in organising thoughts for a useful conceptual model is the development of a diagram along the lines of Figure 60.

The following step involves formalising the sources, affected media, transport mechanisms, exposure media, exposure route, and finally receptors, as in Figure 59.

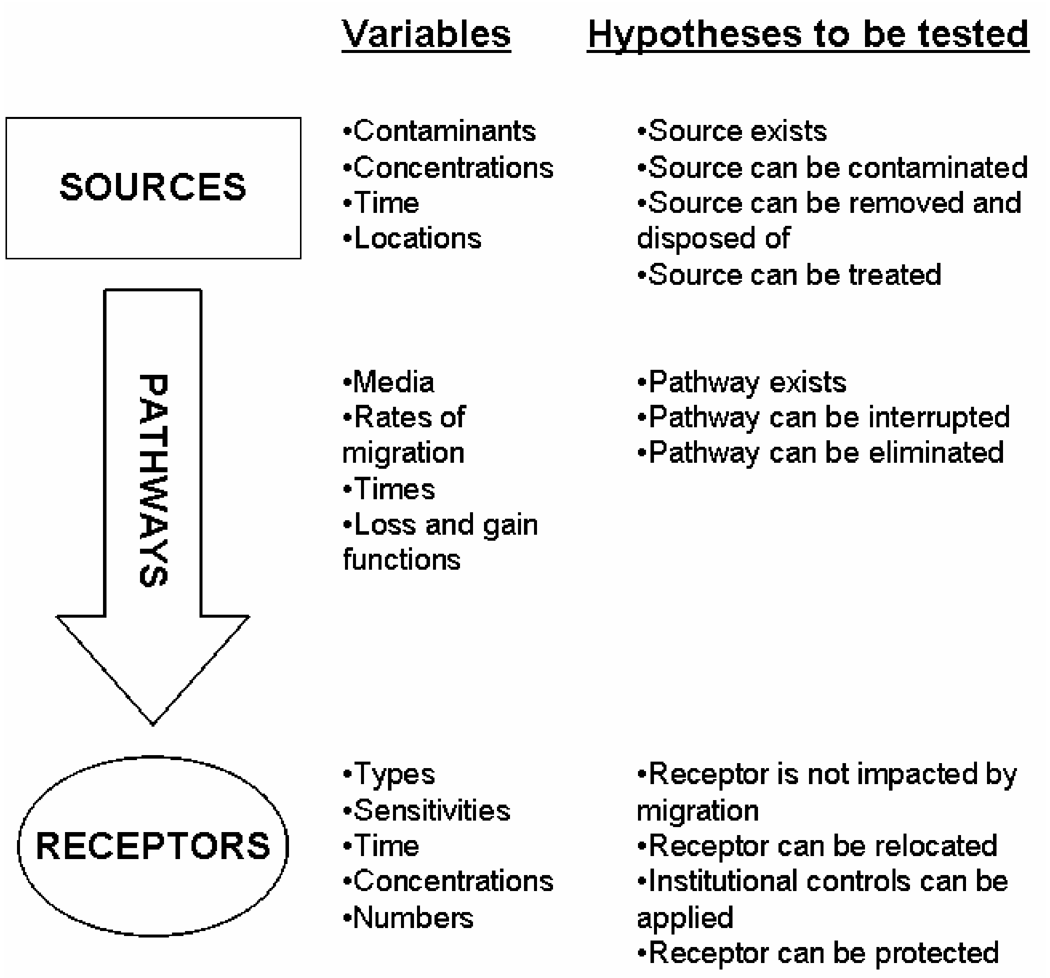

Figure 59: Aid to identifying components of the conceptual model (after USEPA, 1989a)

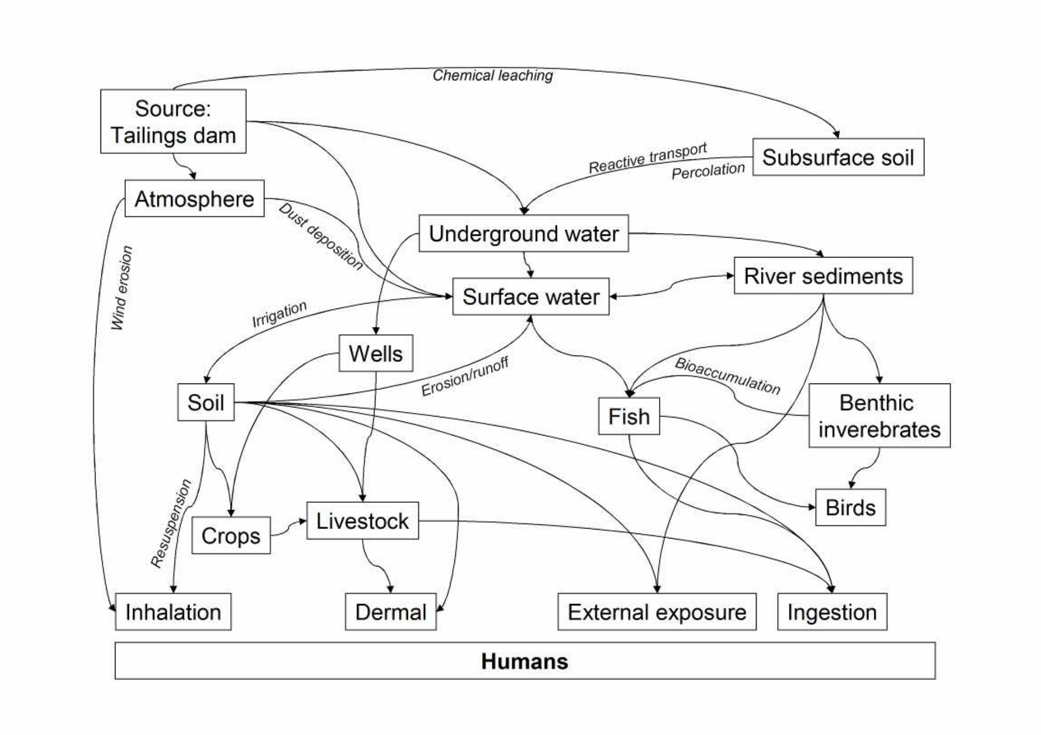

Figure 60: Preliminary graphical conceptual site model (after Servant, 2002) (some pathways investigated in this report are not shown)

9.3.3 Process model

The components of an ecosystem can be divided into several major compartments (Figure 61). None of the environmental compartments exist as separate entities; they have functional connections or interchanges between them. Figure 61 also shows the transport pathways between the released uranium and the environmental compartments, as well as the mechanisms that lead to intakes by the population. 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.

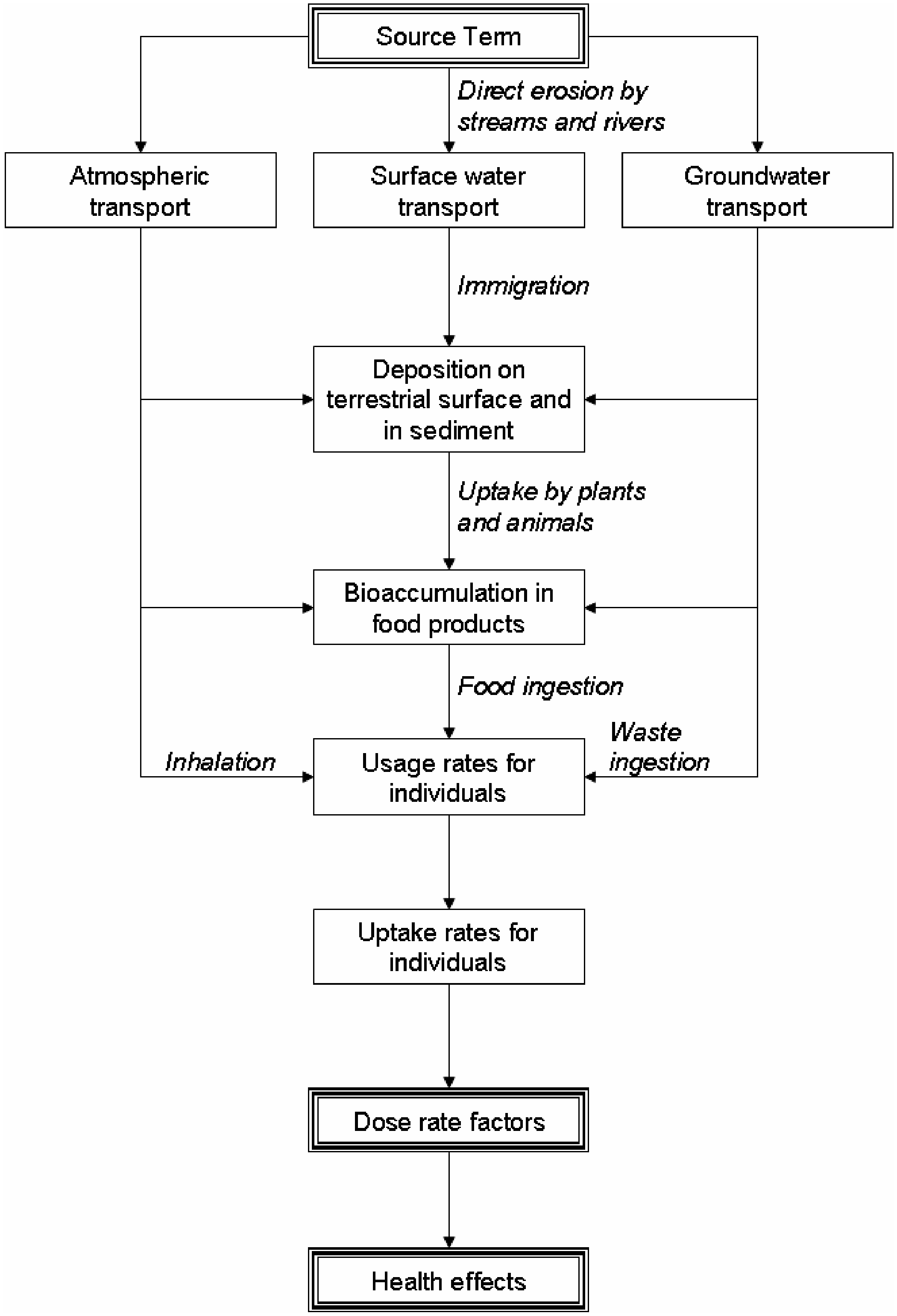

Figure 61: Environmental pathways for potential health effects of uranium (after NCRP, 1984b).

Natural processes of wind and water erosion, dissolution, precipitation, and volcanic action acting on natural uranium in rock and soil, redistribute far more uranium in the total environment than the industries that release uranium to the environment (ANZECC, 2000). These industries may, however, release large quantities of uranium in specific locations, mainly in the form of solids placed on tailings piles, followed by liquids released to tailings ponds and then airborne releases, both directly from the facilities and by wind erosion of the tailings piles. Although solid releases represent the largest quantity of uranium redistribution, they remain on the facility grounds and are normally inaccessible to the public. It is the airborne (direct and wind erosion on tailings piles) and liquid releases (tailings pond run-off and water erosion of tailings) which most likely represent the important pathways for public exposure (i.e. inhalation and ingestion) if pathways can be completed.

The Process Model (as in Figure 62) is a graphical representation of the sources, pathways, mechanisms and sinks in a risk assessment. The representation can be produced in parallel with the steps in generating a conceptual model. The purpose of this model is communication with I and APs. For those project personnel who have more of a visual orientation, the development of this model may assist in identifying pathways and receptors.

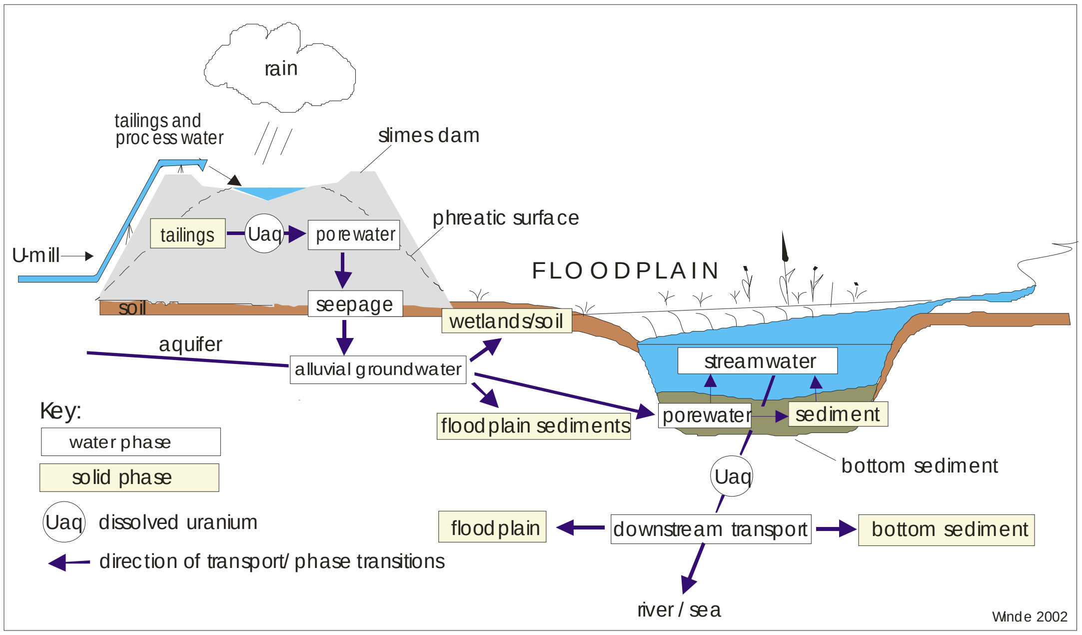

Figure 62: Schematic conceptual site model (from Winde, 2002)

When the conceptual site model is complete, it is used to fill in RAGS Table 1, which, although titled: “Selection of Exposure Pathways for the Wonderfonteinspruit Catchment” is more an *identification* of exposure pathways (Table 12).

9.4 Identification of chemicals of potential concern

9.4.1 Process issues

It is a very rare occurrence that a risk assessment is made without a hypothesis of contamination. Often a risk assessment has been instigated as a result of the activities of a pressure group, and there can be a lot more heat than light in debates on the presence of chemicals of potential concern (COPCs).

Critical to the successful identification (or verification of the existence) of COPCs are considerations of quality control, which are informed by the decision on the scope of the risk assessment taken in Section 1.6.

A useful template for guiding the processes for identifying the COPCs is presented in Figure 63.

Questions to ask in characterising the source (in part from Barnthouse and Brown, 1994):

- What is the source? Is it anthropogenic, natural, point source, or diffuse non-point?
- What type of stressor is it: chemical, physical, or biological?
- What is the intensity of the stressor (e.g. the dose or concentration of a chemical, the magnitude or extent of physical disruption, the density or population size of a biological stressor)?
- What is the mode of action? How does the stressor act on receptors in the study area?

These questions assist in developing the RAGS Table 2 “Occurrence, Distribution, and Selection of Chemicals of Potential Concern (COPCs)”.

Each RAGS Table 2.n should represent a unique combination of Scenario Timeframe, Medium and Exposure Medium.

The RAGS tables have been filled in for water ingested from the river (Table 11).

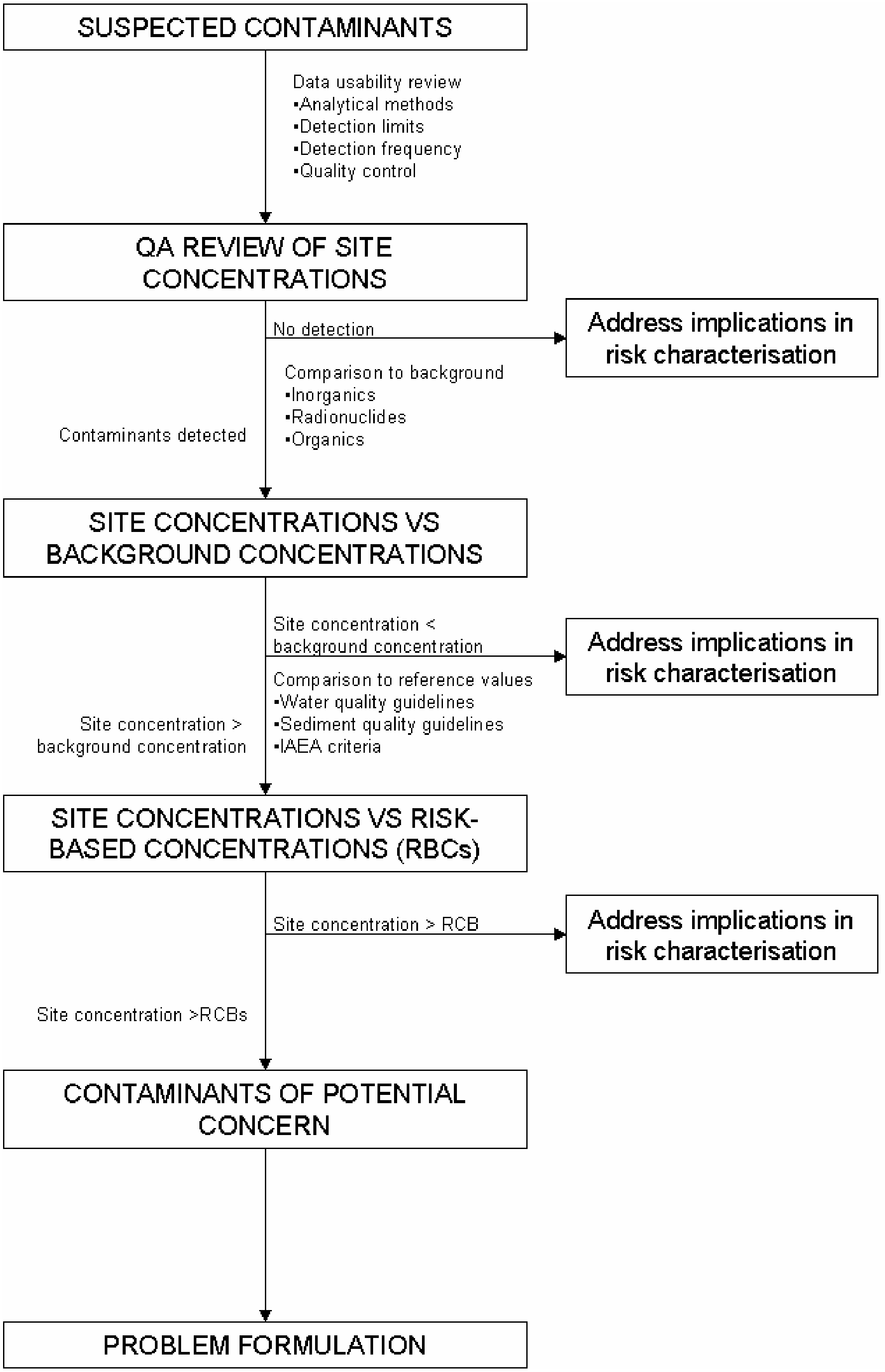

Figure 63: Flowchart for the selection of contaminants of potential concern (COPCs) (after USEPA, 1997b)

9.4.2 Source characterisation

Overview of sources

During the preparation of the conceptual model of the site of interest, sources are identified.

Sources of pollution are described in Section 3.

Data -ollection considerations

Types of data collected

Two sets of data were collected for this study:

- A reconnaissance sampling programme was undertaken and samples analysed using semiquantitative ICPMS scans. These results were used to identify contaminated sites, as well as the contaminants of concern.

- A second set of samples were then collected and analysed quantitatively using XRF, to give accurate precise results.

A number of specialised datasets were collected:

- Sequential chemical extractions were performed on a suite of samples in an attempt to identify the speciation of the contaminants of concern.

- Isotopic studies were undertaken in an attempt to characterise the pollution mechanisms and, where possible, to identify individual polluters.

- A continuous water-quality monitoring study was undertaken in the Wonderfonteinspruit to determine the variability of geochemical conditions at a site in the catchment. This also assisted with characterisation of the range of environmental conditions which may exist within the catchment.

Reconnaissance sampling ─ first phase

A reconnaissance sampling exercise was undertaken in 2001, with the aim of identifying contaminated sites, as well as identifying the priority contaminants in the catchment. Samples were collected at sites throughout the catchment, as well as a background sediment sample from Klerkskraal Dam. Klerkskraal Dam was selected as a background site as it is situated in similar geology to the Wonderfonteinspruit, but has no direct waterborne impacts from gold/uranium mining. There is, however, a possibility of some windblown contamination from slimes dams in the catchment.

Samples were collected at the sites listed in Table 2.

The data are presented in Figure 6 to 11.

Data-evaluation considerations

Issues relating to background concentrations

Issues relating to background concentrations are discussed in Section 4 of this report.

Tier-I risk assessment of sediments

A Tier-I risk assessment of sediments was performed, as in Section 4.1 of this report.

Concentrations and tier-1 risk quotients (depicted with shading) for selected metals from the reconnaissance sampling programme are presented in Table 25.

These data are summarised in Figure 6.

BCR Protocol sequential extraction

Philosophy and method of sequential extractions are described in Section 7 and graphically described in Figure 19.

9.4.3 Identification of contaminant 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 the various studies (IWQS, 1999; Wade et al., 2002; Coetzee et al., 2002), 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.

9.4.4 Summary of chemicals of potential concern

Rags Table – Occurrence, distribution, and selection of chemicals of potential concern (COPCs)

Table 11: RAGS Table 2.1: Occurrence, distribution and selection of chemicals of potential concern in the Wonderfonteinspruit catchment

Exposure point	CAS number	Chemi-cal	Minimum concentration	Maximum concentration	Units	Screening ttoxicity value (N/C)	COPC Flag (Y/N)
Drinking water (river)*	7440611	Uranium	0,01	0,14*	mg/l		Y
	7440611	Uranium 238			pCi/l		Y

* The maximum concentration of uranium in river water used was found in a grab sample taken by Winde in February 2000 during a rain-triggered flood event in the upper Wonderfonteinspruit. It is, however, unlikely that this value constitutes a genuine maximum owing to possible dilution of contaminated stream water by (less or un-contaminated) rainwater. Carter (1997) reports a maximal U238 concentration of approximately *0,4 mg/l* found in weekly samples taken in the upper part of the stream at DWAF station C2H152 from February to August 1997 as part of the afore-mentioned DWAF study into possible uranium contamination of the Wonderfonteinspruit; IWQS, 1999). For water discharged from mines into canals that finally reach the Wonderfonteinspruit a maximum uranium concentration in the same study of **3 mg/l** was found (Carter, 1997: C2H159, Doornfontein GM metallurgical plant effluent). Having observed that water from mine canals is used by local residents of informal settlements, such water also needs to be included in a risk assessment. Regarding the data obtained during the afore-mentioned study it needs to be stressed that only weekly grab samples were taken which do not take account of pronounced temporal fluctuations of uranium concentrations in fluvial systems as described in Chapter 8

(Temporal variation in hydrochemistry of stream water ─ results of a continuous monitoring study (F. Winde, H. Coetzee and G. Ntsume)), as well as Winde, 2003 and Winde et al., 2004a/b.

In addition, Coetzee et al., 2003 report a uranium concentration in a surface-water body next to the northern watershed of the headwater region of the Wonderfonteinspruit (Robinson Lake) of 16 mg/l after underground mine water decanting into the Tweelopiesspruit was pumped into the lake. This extreme concentration is believed to be the result of remobilisation of uranium from a contaminated sediment by acidic water.

9.5 Environmental chemistry of uranium

9.5.1 Atmospheric processes

Emissions of uranium

The presence of uranium and uranium compounds in the atmosphere of the Wonderfonteinspruit catchment results from activities associated with gold mining, probably the bulk of the uranium source located in tailings dams.

Uranium transformation and transport

There is limited information available regarding the abiotic transformation and degradation of uranium and uranium compounds, except for uranium hexafluoride, presumably due to its importance in the nuclear industry. Uranium hexafluoride immediately hydrolyses on contact with moisture in the air to form uranyl fluoride (UO_2F_2) and hydrofluoric acid (HF). It is reasonably certain that this compound is not emitted in the Wonderfonteinspruit catchment.

While entrained in the air, particulate uranium represents an inhalation source for humans, the extent of which is dependent upon concentration and particle size. For particulate uranium to be an inhalation hazard to humans, the particulates must be in the size range of 1–10 µm (ICRP, 1979).

Deposition of uranium

Deposition of the atmospheric uranium can occur by dry deposition or wet deposition (Essien et al., 1985). Dry deposition results from gravitational settling, and thus rate of dry deposition is dependent upon particle-size distribution, chemical form, particle density, and degree of air turbulence (ATSDR, 1999).

Data on the particle size and residence time of uranium and uranium compounds present in ambient atmospheres are not available. Uranium particles are, however, expected to behave like other particles for which data are available, which show that smaller particles (<5 µm) travel longer distances than larger particles because of their longer residence time in the atmosphere due to their low settling velocity.

The chemical form of the uranium affects the atmospheric residence time. One uranium compound for which there is data regarding residence time and particle size is uranium hexafluoride, a soluble compound, which will hydrolyse in the atmosphere to particulate $UO_2F_2 \cdot nH_2O$ and hydrogen-fluoride gas (Bostick et al., 1985). In the case of UO_2F_2, although the particles were small (<2,5 µm), its atmospheric residence time was estimated to be only 35 minutes as a result of rapid hydration and agglomeration to larger particles that have faster settling velocities (Bostick et al., 1985). While uranium hexafluoride is unlikely to be a constituent of the Wonderfonteinspruit catchment, these data do imply that if dust containing uranium is airborne, and is particularly hydrophobic (as in e.g. a silica matrix), it is expected to be transported far, owing to its long atmospheric residence time.

In wet deposition of airborne contaminants, the uranium is washed from the atmosphere by rain, sleet, or other forms of moisture. The rate of wet deposition depends upon particle size and solubility (chemical form). Uranium thus deposited (dry or wet) will usually reside on land or be deposited on surface waters.

Re-emissions of uranium into the atmosphere

If land deposition occurs, the uranium can incorporate into the soil or adhere to plant surfaces, be resuspended in the atmosphere as a result of wind action, or be washed from the land into surface water and groundwater. Resuspension factors are typically quite low (10^{-6}) and protective against significant exposures, but this may not apply to windy and arid areas (ATSDR, 1999). Resuspension into the air can be an inhalation source even after the plume or source has disappeared.

9.5.2 Aquatic processes

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 (Langmuir, 1978). 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 (Langmuir, 1978; Osmond and Ivanovich, 1992).

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 (Choppin and Stout, 1989).

Uranyl hydroxides

The free hydrated uranyl ion (UO_2^{2+}) is the predominant species at pH ≤ 5, but is insignificant at pH ≥ 6 ($U < 10$ µg/L ─ Grenthe et al., 1992). Uranyl ions start to hydrolyse at about pH 3. The concentration of UO_2OH^+ is of secondary importance to UO_2^{2+} at pH ≤ 5, but increases in importance up to pH 6 (Grenthe et al., 1992). The formation of polymeric uranyl-hydroxide complexes, including $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_3(OH)]^{5+}$, $[(UO_2)_4(OH)]^{7+}$ and $[(UO_2)_3(OH)_7]^-$, also increases in importance at pH ≥ 5, particularly at higher uranium concentrations (i.e. >200 µg/L) (Grenthe et al., 1992). At pH 5–6, $(UO_2)_3(OH)^{5+}$ is predicted to be the dominant polymeric uranyl-hydroxide species (Grenthe et al., 1992), whereas from pH 6–8, $[(UO_2)_3(OH)_7]^-$ is predicted to become the most important species (Palmer and Nguyen-Trung, 1995).

Uranyl carbonates

Carbonate complexes of uranium dominate in oxidised fresh surface waters (Clark et al., 1995). At pH 5–6, in moderate to hard waters, the dominant uranium species is $[UO_2CO_3]$, while at pH 6–8 $[UO_2(CO_3)_3]^{4-}$ is the dominant species (Langmuir 1978; Grenthe et al., 1992). The mixed uranyl-hydroxide-carbonate species, $[(UO_2)_2(OH)_3CO_3]^-$, increases in importance with increasing dissolved uranium concentration at pH>8. At pH>10, $[UO_2(OH)_3]^-$ is generally considered to be the dominant uranyl species (Grenthe et al., 1992).

Uranyl complexes with carbonate and phosphate dominate over complexation of uranyl by chloride, sulphate, nitrate and silicate in fresh-water systems (Gascoyne, 1992). Uranyl-phosphate complexes are usually of minor importance in most fresh surface waters, unless the concentration of phosphate approaches 75 µg/L (Langmuir, 1978).

Bernhard et al. (1996) found evidence, through spectroscopic investigation for the existence in mine tailings seepage water, of a uranium-solution species of both calcium and carbonate, $Ca_2[UO_2(CO_3)_3]_{aq}$. A significant aspect of their study was that they found reason to exclude calcium uranate ($CaUO_{4(s)}$) from their chemical- modelling investigation. The existence of this species in environmental conditions was questioned in Wade et al. (2002), and the presence or absence of it had a significant effect on the results of chemical modelling at high pH.

Binding with organic matter

In addition to carbonate, natural organic matter (OM) is a very effective complexing agent of uranium in natural waters (Choppin and Stout, 1989; Moulin et al., 1992). 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 (Livens et al., 1996), or colloidal. In soft, low-alkaline, organic-rich, fresh surface waters (pH 5−7), uranyl-DOM complexes are the dominant species of dissolved uranium. OM complexation increases with increasing pH, owing to increasing ionisation of the carboxylate functional groups of OM (Choppin and Stout, 1989). Conversely, uranyl-OM complexation decreases with increasing uranium concentration (as the surface sites on the OM are saturated).

As the hardness, alkalinity and pH of the water increase (usually pH >7–8), uranyl carbonate and uranylhydroxide-carbonate species become more important than uranyl-OM complexes (Moulin et al., 1992).

Uranyl peroxospecies

In the photic zone, where an elevated concentration of hydrogen peroxide (H_2O_2) is found, uranium shows a strong binding affinity for the peroxide ligand, forming minor proportions (usually <15%) of $[UO_2(CO_3)_2(HO_2)]^{3-}$ (Djogic and Branica, 1993). The photic zone is also relatively rich in natural DOM, with uranyl-DOM complexes forming a component strongly dependent on the concentration of DOM (usually <20% of the dissolved uranium concentration) (Mann and Wong, 1993).

Sorption of uranyl species

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, montmorillinite), 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 (Prikryl et al., 1994; Waite et al., 1994; Kohler et al., 1996; Turner et al., 1996). Sorption of uranium to insoluble organic matter, or organic matter attached to particles (e.g. hydrous iron oxides), also reduces the mobility of uranium (Pompe et al., 1996). Sorption of uranium to particles increases with increasing pH until a threshold point is reached (Willett and Bond, 1995), which varies as a function of the concentration of uranium, adsorbent competing ions (e.g. carbonate), other chelating agents and ionic strength (Dzombak and Morel, 1990).

Solubility, sorption and salinity

In fresh surface waters at pH 6–8, the solubilities of uranyl minerals are near their minimum (Langmuir, 1978) and the sorption of uranyl by organic matter near its maximum (Choppin, 1992). Sorption of uranium to particles and organic matter decreases with increasing salinity (Van den Berg, 1993).

9.5.3 Terrestrial and aquatic fate of uranium

Uranium in the fresh-water ecosystem

The principal abiotic processes that transform uranium in water are formation of complexes and oxidation/reduction. In fresh water at pH 6, U(IV) exists entirely as hydroxocomplexes, and UO_2^{+2} exists as hydrated complexes (12%), hydroxocomplexes (18%), fluorocomplexes (8%), and carbonatocomplexes (60%) (Boniforti, 1987) (Author's note – Boniforti's water sample must have had an unusually high concentration of fluoride). In fresh water at pH 9, U(IV) exists entirely as hydroxocomplexes, but UO_2^{+2} exists as 100 per cent carbonatocomplexes (Boniforti, 1987).

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.

Uranium in sediment

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.

Factors that control the mobility of uranium from sediment to the water phase are the oxidation-reduction potential, the pH, the characteristics of complexing agents or ligands, and the nature of sorbing materials in the water. Inorganic or organic ligands that can form soluble complexes with uranium will result in mobilisation of the uranium in water. The stability of such complexes is dependent on the pH. For example, uranium is likely to be in solution as a carbonate complex in oxygenated water with high alkalinity (Herczeg et al., 1988); however, in acidic waters (pH <6 containing low concentrations of inorganic ions and high concentrations of dissolved organic matter), the uranium is in solution as the soluble organic complex (Brunskill and Wilkinson, 1987).

The oxidation-reduction potential of water is important in controlling the mobility of uranium; in anoxic waters, where the aquatic environment is reductive, U(VI) will be reduced to U(IV) (e.g. changed from a soluble compound to an insoluble one). The U(IV) will be deposited into the sediment because of the insolubility of the resulting U(IV) salts (Allard et al., 1979; Herczeg et al., 1988). Mobilisation and deposition of uranium as defined by the oxidation-reduction potential of the water has been observed by several investigators (Barnes and Cochran, 1993; Shaw et al., 1994).

Uranium in soil

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 (Ames et al., 1982).

Migration of uranium in soil and subsoil, and uptake in vegetation, are usually quite local, involving distances from several centimetres to several metres. In most waters sediments act as a sink for uranium, and the uranium concentrations in sediments and suspended solids are several orders of magnitude higher than in surrounding water (Brunskill and Wilkinson, 1987; Swanson, 1985).

Significant reactions of uranium in soil are formation of complexes with anions and ligands (e.g. CO_3^{-2}, OH^{-1}) or humic acid, and reduction of U(VI) to U(IV). Factors controlling the mobility of uranium in soil and its vertical transport (leaching) to groundwater are the oxidation-reduction potential, the pH, concentration of complexing anions, porosity of the soil, soil-particle size, and the sorbing characteristics of the soils (Allard et al., 1979, 1982; Brunskill and Wilkinson, 1987; Herczeg et al., 1988; Premuzie et al., 1995), as well as the amount of water available (Allard et al., 1982).

Retention of uranium by the soil may be due to adsorption, chemisorption, ion exchange, or a combination of mechanisms (Allard et al., 1982). Any soil property that alters the sorption mechanism will also alter the mobility of uranium in the soil. The sorption of uranium in most soils is such that it may not leach readily from soil surface to groundwater, particularly in soils containing clay and iron oxide (Sheppard et al., 1987), although other geological materials such as silica, shale, and granite have poor sorption characteristics (Erdal et al., 1979; Silva et al., 1979). Sorption in most soils attains a maximum when the neutral hydroxyl complex of uranium is at a maximum.

At pH 6 and above, in the presence of high carbonate or hydroxide concentrations, however, uranium may form anionic complexes such as $[UO_2(OH)_4]^{-2}$. The mobility of anionic uranium complexes in soil is dependent upon the nature of the soil. For example, a decrease in sorption in soil with little anion-exchange capacity may result in increased mobility, and increased sorption in soil with high anion exchange may result in decreased mobility (Allard et al., 1982; Ames et al., 1982; Brookins et al., 1993; Ho and Doern, 1985; Hsi and Langmuir, 1985).

Other factors also affect the mobility of uranium in soil. A field study done near an active carbonate-leach uranium mill showed that uranium in an alkali matrix can migrate to the groundwater (Dreesen et al., 1982), presumably as a charged, soluble carbonate species (Author's note).

Plant and animal uptake of uranium

Uranium mobility may also be increased owing to the formation of soluble complexes with chelating agents produced by micro-organisms in the soil (Premuzie et al., 1995). 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.

The plants, aquatic or terrestrial, may be eaten directly by humans, or consumed by land or aquatic animals which provide food for humans. The uptake or bioconcentration of uranium by plants or animals is the mechanism by which uranium in soil, air, and water enters into the food chain of humans.

The primary abiotic and biological processes that transform uranium in soil are oxidation-reduction reactions that convert U(VI) (soluble) to U(IV) (insoluble). Reduction of U(VI) to U(IV) can occur as a result of microbial action under anaerobic soil or sediment conditions, thereby reducing the mobility of uranium in its matrix (Barnes and Cochran, 1993; Francis et al., 1989). Further abiotic and biological processes that can transform uranium in the environment are the reactions that form complexes with inorganic and organic ligands. Certain micro-organisms (e.g. *Thiobacillus ferrooxidans*) facilitate the oxidation of Fe^{+2} to Fe^{+3}. The Fe^{+3} ion, in turn, can convert insoluble uranium dioxide to soluble UO_2^{+2} ions by the following reaction: $2Fe^{+3} + UO_2 \rightarrow UO_2^{+2} + 2Fe^{+2.}$ This reaction enhances the mobility of uranium in soil from mining and milling wastes (Barnes and Cochran, 1993; De Siloniz et al., 1991; Scharer and Ibbotson, 1982).

Uranium may be removed from the pore water of sediments under sulphate-reduction conditions; microbes may control this process indirectly (Barnes and Cochran, 1993).

Numerous factors influence the bioaccumulation of uranium, such as the chemical and physical form of the uranium; the season of the year and other climatic factors such as temperature, age of the organism, specific tissue or organs involved; and the specific characteristics of the local ecosystem, such as total suspended and dissolved solids. Bioconcentration factors for uranium have been measured by several investigators in various aquatic organisms. Mahon (1982) measured bioconcentration factors of 1 576 and 459 in algae and plankton, respectively. Bioconcentration factors have been measured in several species of bacteria that ranged from 2 794 to 354 000. Bioconcentration by the bacteria represented adsorption onto the cell surfaces of the bacteria rather than true biological uptake (Horikoshi et al., 1981).

Low bioconcentration factors for uranium have been observed in fish. The highest bioconcentration factors observed in fillet of rainbow trout *(Salmo gairdneri)*, white and finescale suckers *(Castastomus catactomus)*, and lake whitefish *(C. clupeaformis)* did not exceed a value of 38 (Mahon, 1982; Poston, 1982; Swanson, 1983; 1985). The primary source of uranium for crab *(Pachygrapsus laevimanus)* and zebra winkle *(Austrocochlea constricta)* was from the water column, since both fed and starved animals took up uranium at the same rate (Ahsanullah and Williams, 1989).

Uranium uptake from soils to plants is poor (Dreesen et al., 1982; Moffett and Tellier, 1977). As with aquatic organisms, the uptake of uranium by plants is dependent on the nature of the soils (soil texture and organic content), the pH, and the concentration of uranium in the soil. Greater plant uptake is expected to occur in soils that contain higher levels of available uranium (i.e. less sorption of uranium to soil particles, or preferential formation of soluble uranium complexes). Swiss chard grown in sandy soils contained 80 times the levels of uranium found in Swiss chard grown in peat soil (Sheppard et al., 1983). The uptake of uranium by native plants, expressed as plant:soil concentration ratio (CR), grown near a mining and milling complex was 0,8 compared with a CR of 0,09 for plants grown in soil with background levels of uranium (Ibrahim and Wicker, 1988). Reported CR values for plant/soil interaction vary widely (range, 0,0025–0,81) (Ibrahim and Wicker, 1988; Mortvedt, 1994). It is of note, however, that Schoonbee et al. (1995) report up to 100 mg/kg of uranium in reeds of the *Cartensis* genus in the East Rand Goldfields.

Although some studies indicate that CR values in plants do not vary linearly with the concentration of uranium in the soil (Mortvedt, 1994), other reported studies show a linear relationship between plant content and soil content of uranium (NCRP, 1984). Uranium uptake by plants may be limited to the outer membrane of the root system and may not occur on the interior of the root at all (Van Netten and Morley, 1983; Sheppard et al., 1983). However, other investigators have reported the transfer of uranium from soil to the stems and leaves of plants in which the CR decreased in the following order: fruit < leaf < root (Morishima et al., 1977). Because of the higher root sorption of uranium, consumption of radishes and other root vegetables grown in uranium-containing soils may be a source of human exposure (Van Netten and Morley, 1983).

Biotic fate of uranium

Bioavailable species of uranium

It is generally considered that UO_2^{2+} is the form of uranium(VI) primarily responsible for eliciting a toxic response in aquatic organisms. It has been suggested that the hydrolysed complex UO_2OH^+ also elicits a toxic response (Markich et al., 1996). This may be due to conversion of UO_2OH^+ to UO_2^{2+} at the biological uptake site (Author's note). Typically, inorganic and organic complexes of uranium(VI) ameliorate the uptake and toxicity of uranium(VI) by reducing the concentration of UO_2^{2+}. Several studies have established that uranium toxicity is inversely related to water hardness (Parkhurst et al., 1984; Poston, 1982). These studies confounded the effects of true water hardness (calcium and/or magnesium concentration) with alkalinity and pH, since an increase in calcium and/or magnesium concentration is frequently associated with an increase in alkalinity (as calcium and/or magnesium carbonate), and hence, pH, and are thus not definitive.

Markich et al. (1996) showed that the toxicity of uranium to a fresh-water bivalve (*Velesunio angasi*) was inversely proportional to alkalinity, where both pH and water hardness were held constant. Geochemical speciation modelling of the water chemistry showed that uranium toxicity was inversely proportional to the percentage of UO_2CO_3 present; hence, UO_2CO_3 was not considered toxic (see Poston, 1982). Complexation of uranium by carbonate reduces the concentration of the free hydrated uranyl ion (UO_2^{2+}).

Effects of pH on uranium toxicity

The uptake and toxicity of uranium is inversely related to pH, over the range 2–7, at constant water hardness and alkalinity (Markich et al., 1996). The sublethal toxicity of uranium to *V. angasi* in a synthetic water is about five times greater at pH 5 (48 h EC_{50} = 117 µg/L) than at pH 6 (48 h EC_{50} = 634 µg/L). The change in pH (H^+) over this range also results in a large change in the speciation of uranium, as predicted by geochemical speciation modelling. The influence of pH *per se* on organism response between pH 5 and 6 is minimal, and thus changes in uranium speciation were responsible for the observed toxicity of uranium (Markich et al., 1996).

Chemical speciation modelling predicts that, as the pH increases from 5 to 6, the relative proportions of UO_2^{2+} and UO_2OH^+ decline, while the proportions of several uranyl-hydroxides ($[(UO_2)_3(OH)_5]^+$ and $[(UO_2)_3(OH)_7]^-$, and a mixed uranyl-hydroxide carbonate $[(UO_2)_2(OH)_3CO_3]^-$) increase. In contrast, over a wider pH range (2–7), the binding of uranium to *Chlorella* sp. seems to be inhibited at low pH by protonation of weakly basic binding sites on the algal surface. The reduction of uptake and toxicity of uranium to (semi-) aquatic organisms by water-soluble organic ligands has been demonstrated by Markich et al. (1996).

Effects of organic ligands

Organic ligands, including citrate, aspartate, malonate, salicylate and tricarballyate (collectively used as a model fulvic acid), ameliorate uranium toxicity by complexing *cationic* uranyl species (e.g. UO_2^{2+} and UO_2OH^+) (Markich et al., 1996). In contrast, the complexation of uranyl with oxalate to form complexes of $[UO_2Ox_2]^{2-}$ *enhances* the toxicity of uranium (Boileau et al., 1985). This may be due to the formation of complexes, the shape of which are similar to that of an environmental micronutrient, thus enhancing uptake of uranium, and is unlikely to be a general phenomenon in the bioavailability of uranium with small organic ligands (Author's note).

Using a linear regression technique that plotted the predicted uranium speciation as a function of biological response to uranium over a range of pH (5–6) and organic acid (simulated fulvic acid) concentrations (3,2–7,5 mg/L), Markich et al. (1996) concluded that ~96 per cent of the biological response could be explained by the percentage sum of $2 \times UO_2^{2+} + UO_2OH^+$. No studies have reported the bioavailability of uranium sorbed to colloidal and/or particulate matter.

Effects of water hardness

Although evidence exists to indicate that the uptake and toxicity of aluminium, chromium(VI), uranium and vanadium in fresh-water organisms is reduced with increasing water hardness, insufficient data are currently available to develop hardness-dependent algorithms.

The reported decreases in the uptake and toxicity of uranyl could be attributed to:

- a reduction in the concentration of the free hydrated uranyl ion (UO_2^{2+}), resulting primarily from an increase in the formation of uranyl carbonate complexes (Poston, 1982); and/or

- an increase in Ca^{2+} and/or Mg^{2+} that may compete with UO_2^{2+} for binding and transport sites at the cell surface of organisms, without directly changing the speciation of uranium in the water (Markich and Jeffree, 1994).

9.6 Exposure assessment

9.6.1 Characterisation of exposure setting

Physical setting
The physical setting of the study site is described in Section 2.

Potentially exposed populations
Relative locations of populations with respect to site
The Wonderfonteinspruit valley is densely populated owing to its agricultural value and the presence of gold mines.

Potchefstroom is located downstream of the Wonderfonteinspruit, from which approximately 400 000 people derive their drinking water via the Boskop and Potchefstroom Dams.

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.

9.6.2 Identification of exposure pathways

Sources and receiving media
A mind-map of the sources, transport pathways and receiving media is prepared to assist with identifying important contaminant routes.

Overview of sources
Sources of uranium are discussed in Section 3.2.

Pathways and mechanisms of uranium migration from mining sources into the environment
Pathways and mechanisms of migration of uranium are discussed in Section 2.

9.6.3 Fate and transport in release media

An extensive analysis of the fate and transport of uranium in the release media is presented in Sections 3.3, 3.4 and 3.5.

Radiological uranium exposure

In some cases, the solid tailings have been removed from the site for use as fill or construction material, which can lead to external radiation exposures primarily from the uranium progeny.

Summary of exposure pathways to be quantified in this assessment

The integration of sources, releases, fate and transport mechanisms, exposure points and exposure routes into complete exposure pathways was performed, and presented as Rags Table – "Selection of Exposure Pathways (Table 12). In this study, only the water pathway has been studied.

Table 12: RAGS Table 1: Selection of exposure pathways for the Wonderfonteinspruit catchment

Scenario timeframe	Medium	Exposure medium	Exposure point	Receptor population	Receptor age	Exposure route	Type of analysis	Rationale for selection or exclusion of exposure pathway
Present	Atmosphere	Air	Air	Resident	Child/Adult	Inhalation	Quant	Onsite residents may breathe in suspended dust particles
		Surface water	Drinking water	Resident	Child/Adult	Ingestion	Quant	Onsite residents may rely on water from the rivers
		Surface water	Swimming water	Resident	Child/Adult	Dermal	Quant	Onsite residents may swim in the rivers/dams
		Fish tissue	Edible fish – contaminant uptake from surface water	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest local food products
	Surface water	Air	Water vapours from shower head	Resident	Child/Adult	Inhalation	Quant	Onsite residents may rely on water from the rivers
		Surface water	Drinking water	Resident	Child/Adult	Ingestion	Quant	Onsite residents may rely on water from the rivers
		Surface water	Swimming water	Resident	Child/Adult	Dermal	Quant	Onsite residents may swim in the rivers/dams
		Fish tissue	Edible fish – contaminant uptake from surface water	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest local food products
	Groundwater	Air	Water vapours from shower head	Resident	Child/Adult	Inhalation	Quant	Onsite residents may rely on domestic wells drawing from Aquifer
		Groundwater	Aquifer – Tap water	Resident	Child/Adult	Ingestion	Quant	Onsite residents may rely on domestic wells drawing from Aquifer
		Groundwater	Aquifer – Tap water	Resident	Child/Adult	Dermal	Quant	Onsite residents may bath

Scenario timeframe	Medium	Exposure medium	Exposure point	Receptor population	Receptor age	Exposure route	Type of analysis	Rationale for selection or exclusion of exposure pathway
		Soil	Soil in Wonderfonteinspruit	Resident	Child/Adult	Dermal	Quant	Onsite residents may come into contact with soil.
		Soil	Soil in Wonderfonteinspruit	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest soil.
		Soil	Soil in Wonderfonteinspruit	Resident	Child/Adult	External (radiation)	Quant	Onsite residents may come into contact with radiation emitted by soil.
	Soil	Soil	Soil in Wonderfonteinspruit	Resident	Child/Adult	Dermal	Quant	Onsite residents may come into contact with soil.
			Soil in Wonderfonteinspruit	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest soil.
			Soil in Wonderfonteinspruit	Resident	Child/Adult	External (radiation)	Quant	Onsite residents may come into contact with radiation emitted by soil.
	Sediment	Sediment	River	Resident	Child/Adult	External (radiation)	Quant	Onsite residents may come into contact with radiation emitted by exposed sediment.
			Dam	Resident	Child/Adult	External (radiation)	Quant	Onsite residents may come into contact with radiation emitted by exposed sediment.
		Fish Tissue	Edible fish – contaminant uptake from sediment	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest local food products
	Livestock	Edible portion	Foods	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest local food products
	Crops	Edible portion	Foods	Resident	Child/Adult	Ingestion	Quant	Onsite residents may ingest local food products

9.6.4 Quantification of exposure

Exposure concentrations

Exposure concentrations are presented in Sections 4 and 3.4.

Estimation of chemical intakes for individual pathways

Estimation of chemical intakes are particularly problematic. In the current assessment, it is assumed that people are primarily at risk because of ingestion of uranium by drinking water. Risks associated with the ingestion of riverbank material by young children and pregnant mothers (the practice of geophagy — also known as 'pica' — is widespread in rural African communities) are not quantified. It is worth noticing that uraniferous salt crusts, preferably forming on low-lying floodplain sediments and river banks, were found to contain extremely high concentrations of uranium (up to 1 100 mg/kg; Winde, 2001).

9.6.5 Identification of uncertainties

Environmental sampling and analysis

Because of the great temporal variability, grab samples do not reflect the full range of possible uranium concentrations in water over long-term periods, very likely missing uranium maxima, e.g. at night time and during events.

9.6.6 Summary of exposure assessment

Rags Table - Exposure point concentration (Epc) summary

Table 13: Table 3.1.RME: Exposure point concentration summary

Exposure point	Chemical of potential concern	Units	Maximum concentration*	Exposure point concentration	
				Value	Units
Drinking water (River)	Uranium	µg/L	140	140	µg/L
	Uranium 238	pCi/L			pCi/L

* see remarks on actual maxima found in the Wonderfonteinspruit catchment area and adjacent areas in Section 9.4.4 Summary of chemicals of potential concern.

9.7 *Toxicity assessment*

9.7.1 Health effects of uranium and uranium compounds

The principal radiation given off by uranium is alpha radiation. Since alpha radiation travels the shortest distance of all known forms of radiation, it is only effective as a toxin if it comes into direct contact with living tissue. Thus, the routes of exposure of concern may be limited to inhalation, ingestion and dermal contact. Radiotoxicity is expressed as cancer.

It should be stressed, though, that uranium decays into products that emit beta- and gamma radiation, that are a lot more radiotoxic than the parent uranium.

The principal adverse chemical health effect ascribed to uranium to date has been damage to the kidneys.

Acute and intermediate health effects due to uranium exposure cannot easily be distinguished by mechanism of action (chemical- or radiotoxicological). Therefore, The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 1988) has recommended that hazard determinations be based on *chemical* toxicity, which has been observed in humans and animals, as opposed to *radiotoxicity*, the effects of which are not unambiguous.

The most soluble compounds of uranium have been found to be most toxic. These include uranyl nitrate hexahydrate, uranyl fluoride, uranium tetrachloride, and uranium pentachloride. Uranium in this form is a bone-seeking agent, and the bone is the final repository of most of the soluble uranium. Generally, hexavalent uranium, which forms soluble compounds, is more likely to be a systemic toxicant than the less-soluble tetravalent uranium.

The slightly soluble compounds, such as uranium trioxide, sodium diuranate, and ammonium diuranate, are less toxic. These “less-soluble” compounds (designated solubility type M by the ICRP (1995)), tend to remain in the lungs and associated lymph glands for weeks.

The insoluble compounds, such as uranium tetrafluoride, uranium dioxide, uranium tetrachloride, and triuranium octaoxide have not been found to be chemically toxic.

9.7.2 Minimal risk levels (MRLs) of uranium

“MRLs are not meant to support regulatory action; but to acquaint health professionals with exposure levels at which adverse health effects are not expected to occur in humans. They should help physicians and public health officials determine the safety of a community living near a chemical emission, given the concentration of a contaminant in air or the estimated daily dose in water. MRLs are based largely on toxicological studies in animals and on reports of human occupational exposure.” (ATSDR, 1999).

9.7.3 Health effects by route of exposure

Inhalation exposure

The health effects of uranium particles inhaled seem to depend on two factors ─ the size of the particles, and the water-solubility of the particles (Tannenbaum et al., 1951).

Small particles (≤ 2 µm diameter) are carried by the inhaled air stream all the way into the alveoli (the “deep respiratory tract”). Here the particles can remain for periods from weeks up to years (ICRP, 1994; NCRP, 1997), depending on their solubility. Highly insoluble uranium compounds may remain in the alveoli, whereas soluble uranium compounds may dissolve and pass across the alveolar membranes into the bloodstream, where they may exert systemic toxic effects. In some cases, insoluble particles are absorbed into the body from the alveoli by phagocytosis into the associated lymph nodes.

Larger particles, being more susceptible to gravitational forces, tend to deposit higher in the respiratory tract. They are cleared from the respiratory tract by the formation of mucous, which is swept up into the mouth, and expurgated or swallowed into the gastrointestinal system. The latter fate of the particles is converted from the pulmonary system to the gastrointestinal system. The gastrointestinal system is more chemically aggressive than the pulmonary system, and uranium compounds that wouldn’t dissolve in the lungs may become systemically available due to chemical dissolution in the gut.

Acute pulmonary effects have, however, been ascribed to chemical toxicity as opposed to radiotoxicity of uranium in observations of experiments with rabbits (Morris et al., 1989). However, “insoluble” particles (ICRP type S) may reside in the lungs for years, causing chronic radiotoxicity to be expressed in the alveoli.

The Minimal Risk Level for uranium by inhalation has been derived by the Agency for Toxic Substances and Disease Registry (ATSDR, 1999) and by WISE (2003). The values have been summarised in Table 14.

Table 14: Tolerable air concentration (chemical toxicity) for uranium by inhalation.

	Duration[a]	MRL µg/m^3	Dose end point	Effects on animal	Ref
Uranium (soluble forms)	Intermediate	0,4	LOAEL	0,15 mg/m^3; minimal microscopic lesions in the renal tubules in half the dogs examined. Proteinuria observed at 2,2 mg/m^3, severe renal damage at 9,2 mg/m^3.	Rothstein (1949); ATSDR (1999)
Uranium (insoluble forms)	Intermediate	8	NOAEL	1,1 mg/m^3; (LOAEL for minimal microscopic lesions in the renal tubules observed at 8,2 mg/m^3 in two of six dogs examined).	Rothstein (1949), ATSDR (1999)
Uranium (soluble forms)	Chronic	0,3	NOAEL	0,05 mg/m^3; (minimal microscopic lesions in the renal tubules in dogs of both sexes at a LOAEL of 0,20 mg U/m^3).	Stokinger, (1953b); ATSDR (1999)
Uranium (soluble forms)	Chronic	0,07	NOAEL	40 µg/m^3/day; (slight renal effects in rats at a LOAEL of 0,07 µg U/m^3).	Stokinger, (1953a); WISE (2003)

a) Intermediate: 6 hours/day, 6 days/week – (or 15–364 days (ATSDR, 1999)); Chronic: 365 days or more (ATSDR, 1999).

Table 15: Radiological toxicity for uranium to the public by inhalation (WISE, 2003).

	insoluble			soluble		
	Dose factor [mSv/mg]	ALIa [mg]	DACb [µg/m3]	Dose factor [mSv/mg]	ALIa [mg]	DACb [µg/m3]
natural uranium with progeny	0,70	1,42	0,18	1,6	0,63	0,08
pure natural uranium	0,22	4,5	0,58	0,013	74,5	9,4
enriched natural uranium (3,5%)	0,75	1,34	0,17	0,045	22,3	2,8
depleted natural uranium (0,2%)	0,12	8,3	1,05	0,0075	134	17
recycled uranium	0,71	1,41	0,18	0,081	12,3	1,6
enriched recycled uranium (3,5% equiv.)	3,1	0,324	0,041	0,4	2,49	0,32
depleted recycled uranium (0,2%)	0,19	5,27	0,67	0,012	85,1	11

a) ALI = Annual Limit on Intake based on 1 mSv/a.

b) DAC = Derived Air Concentration based on 1 mSv/a, breathing rate of 0,9 m^3/h, continuous exposure

Short-lived decay products included

Based on ICRP72 dose factors for adults, initial enrichment to 3,5%, burnup of 39 GWd/tHM, storage time of five years after unload

Oral exposure

On average, uranium seems to exert more of a toxic effect per unit dose when administered orally as opposed to by inhalation (ATSDR, 1999). This is ascribed to the comparatively low gastrointestinal uptake of uranium compounds. When uranium is ingested in food or liquids, the bulk of the uranium leaves the body within a few days in the faeces (Author’s note — perhaps uranium is reduced to U(IV) in the stomach, in which form it binds extremely strongly to the phenolic compounds that are refractory to the body’s uptake chemistry). A small fraction (0,1–6%) is taken up into the small intestine, where it partitions among the bones, kidneys and other tissues bearing high molecular-weight proteins.

The Committee on the Biological Effects of Ionizing Radiation (BEIR IV) has reported the development of bone sarcomas in 1–2 out of a million people exposed to oral intake of 1 pCi of uranium every day of their lives for 70 years.

Zamora (1998) studied the effects of chronic ingestion of uranium with drinking water on humans. Kidney function is affected by uranium uptake considered safe in publications based on animal studies (WISE, 2003) — "A study was conducted of the chemical effects on the human kidney induced by the chronic ingestion of uranium in drinking water. Subjects were divided into two groups: The low-exposure group, whose drinking water was obtained from a municipal water system and contained < 1 µg uranium/L, and the high-exposure group, whose drinking water was obtained from private drilled wells and contained uranium levels that varied from 2 to 781 µg/L." These levels caused uranium intakes in the range of 0,004 to 9 µg per kg body weight and day.

From the study's conclusions: “The present investigation suggests that long-term ingestion of uranium by humans may produce interference with kidney function at the elevated levels of uranium found in some groundwater supplies. These observed effects may represent a manifestation of subclinical toxicity which will not necessarily lead to kidney failure or overt illness. It may, however, be the first step in a spectrum which, with the chronic intake of elevated levels of uranium, may lead to progressive or irreversible renal injury." (WISE, 2003).

“In a more recent larger study on humans [Kurttio et al., 2002], nephrotoxic effects of uranium in drinking water were found even for low concentrations — without a clear threshold. The authors conclude that ‘... our results suggest that the safe concentration of uranium in drinking water may be within the range of proposed guideline values of 2–30 µg/L’” (WISE, 2003).

Table 16: Hazard (chemical toxicity) uranium by ingestion (WISE, 2003)

TDI [µg/(kg·d)]	ALI [mg]	DDWC [µg/l]	Ref
2	51,2	102	ATSDR (1999)
0,7	17,9	36	Jacob (1997)
0,6	15,3	31	WHO (1998)

TDI = Tolerable Daily Intake
ALI = Annual Limit on Intake based on 70 kg body weight
DDWC = Derived Drinking Water Concentration based on 500 l/a

Table 17: Hazard (radiological toxicity) to the public for uranium by ingestion (WISE, 2003)

	Dose factor [mSv/g]	ALI [mg]	DDWC [µg/l]
natural uranium with progeny	31,7	31,5	63
pure natural uranium	1,23	813	1 630
enriched natural uranium (3,5%)	3,98	251	500
depleted natural uranium (0,2%)	0,71	1 410	2 820
recycled uranium	3,89	257	515
enriched recycled uranium (3,5% equiv.)	16,7	60	120
depleted recycled uranium (0,2%)	1,08	923	1 850

ALI = Annual Limit on Intake based on 1 mSv/a
DDWC = Derived Drinking Water Concentration based on 1 mSv/a, 500 l/a
Short-lived decay products included
Based on ICRP72 dose factors for adults (these don't make a distinction for solubility), initial enrichment to 3,5%, burnup of 39 GWd/tHM, storage time of five years after unload

Dermal exposure

Uranium seems to behave identically in the transdermally absorbed route to uranium compounds absorbed through the lungs and the gastrointestinal tract (ATSDR, 1999). The more water soluble the compounds were, the more toxic. Death is due to renal failure.

9.7.4 Discussion of health effects by observed symptoms

Death

Owing to the multiplicity of confounding factors, including the mechanical effect of other dust that has been inhaled, fatal toxic effects of uranium-bearing dust inhalation have not been expressed unambiguously in uranium miners (Dockery et al., 1993).

Animals exposed to uranium compounds by the inhalation route have died, the cause of death being traced to damage to the renal system.

Uranium compounds seem to have a low order of mammalian toxicity by the inhalation, oral and dermal routes. No deaths have been unambiguously causally associated with prolonged occupational exposure to inhaled uranium compounds (ATSDR, 1999).

Systemic effects (ATSDR, 1999)

- Respiratory effects: prolonged exposure to high levels of insoluble uranium dust may damage the lungs by chemical action.

- Cardiovascular effects: No unambiguous cardiovascular damage has been associated with uranium exposure.

- Gastrointestinal effects: No gastrointestinal effects have been observed.

- Haematological effects: No haematological disturbances have been associated with uranium exposure.

- Musculoskeletal effects: No musculoskeletal effects have been observed.

- Hepatic effects: Liver dysfunction has only been observed in the case of a person who drank 15 g of the extremely soluble uranyl acetate. Uranium has been found to disrupt general hepatocellular function and cellular permeability in animal studies, but the toxic response of the liver is an order of magnitude lower than that of the kidney.

- Renal effects: Uranium is nephrotoxic, exerting its toxic effect by chemical action mostly in the proximal renal tubules in humans and animals. Discontinuation of exposure to uranium prior to irreversible damage allows the kidney to be cleared of uranium, with concomitant healing of affected sites.

- Endocrine effects: None known.

- Dermal effects: While dermal effects have not been observed in humans, animal experiments involving inoculation with high doses of uranium compounds have produced skin irritation, severe dermal ulcers, or superficial coagulation necrosis, swollen, vacuolated epidermal cells and damage to hair follicles and sebaceous glands.

Immunological and lymphoreticular effects

No adverse immunological or lymphoreticular effects were reported in human studies following exposure to uranium through the inhalation, oral, or dermal route for any duration (ATSDR, 1999). No significant uranium-induced immunological or lymphoreticular changes were observed in animals exposed to uranium for acute, intermediate, or chronic durations.

Neurological effects

Recent studies with rats and military veterans who have uranium embedded in their bodies indicated a high correlation with impaired performance efficiency and uranium loading.

Central-nervous-system toxicity of other heavy metals is well documented, but the subject has not been thoroughly explored with respect to uranium (ATSDR, 1999).

Reproductive effects
"In view of the lack of findings of reproductive effects in uranium miners, millers, and processors in numerous human studies, and the equivocal findings in high-dose animal studies, it is doubtful that human exposure to uranium compounds at or near hazardous waste sites could result in interference with normal reproduction." (ATSDR, 1999).

Developmental effects
Uranium is a DNA-adducting chemical, and is thus expected to act on cells with a high mitotic index, such as those found in the embryo, foetus and neonate, with teratogenic effects. These effects are observed, but "at relatively high doses far above any plausible human exposure" (ATSDR, 1999).

Genotoxic effects
Animal studies with high doses of uranium have indicated a correlation between chromosomal breaks and uranium concentration. Responses are dose and time dependent, and strongly correlated with uranium concentration in urine. ATSDR (1999) notes that these effects appear in cases of high *injected* doses of uranium, and suggests that it is unlikely that humans may experience such high doses via the routes of inhalation, ingestion and dermal exposure.

Cancer
Because of the multiplicity of carcinogenic agents involved in human epidemiological studies, there is no unequivocal evidence that inhalation, or oral or dermal exposure induces cancers in humans. ATSDR (1999) does state that "indications of the cancer- inducing potential of uranium in … [miners, millers, processors] were useful in making a determination that uranium exposure by normal routes of exposure is unlikely to be carcinogenic. … Available long-term animal studies characterise uranium's cancer potential as low."

However, laboratory experiments have revealed that, where there are very high concentrations of uranium in tissues (including bone), prolonged action of the uranium on cells exerts a definite carcinogenic effect (Hueper et al., 1952).

9.7.5 *Regulatory limits*

There is much controversy on the subject of regulatory limits. WISE (2003) notes that there is no information for long-term effects of uranium ingestion on humans, all information currently available being from intermediate-term studies on animals.

Standards for radiation doses and chemical toxicity are not comparable ─ for radiation and for cancer-inducing effects of chemical toxics, a linear dose-effect relationship is assumed at low doses and low dose rates; therefore any standard can only limit the effects to a selected level, while for non-cancer-inducing effects of chemical toxics, the existence of a no-observed adverse-effect level (NOAEL) is assumed. In other words, there is no safe limit for carcinogens.

The residual risk from chemical toxicity regarded as acceptable is usually many orders of magnitude lower than from radiation ─ the lifetime cancer risk from continuous radiation exposure at ICRP's dose-rate standard for the public of 1 mSv/a during a 70-year lifetime is 1:286, and the lifetime cancer risk for workers exposed at ICRP's current dose-rate standard for workers of 20 mSv/a during a 40-year work life is 1:31. These low numbers are not comparable to the acceptable lifetime risk from toxics often selected in the 1:10 000 to 1:1 000 000 range (WISE, 2003).

Inhalation: Current standards (WISE, 2003)

U.S. NRC Occupational Annual Limits on Intake (ALIs) for Inhalation

$U_{natural}$ (soluble): 1 µCi (= 37 000 Bq, equiv. to 1,5 g)

$U_{natural}$ (insoluble): 0.05 µCi (= 1 850 Bq, equiv. to 74 mg)

(10 CFR 20, App. B, 1991)

These values are based on a committed effective dose equivalent of 5 rems (50 mSv).

U.S. NRC Occupational Derived Air Concentrations (DACs)

$U_{natural}$ (soluble): 5.0E-10 µCi per ml of air (= 18,5 Bq/m^3, equiv. to **0,74 mg/m^3**)

To address the chemical toxicity, the following tighter criterion is defined, in addition to the radiological one:

- **0,2 mg uranium/m^3 of air** (for soluble uranium)
- **0,045 mg natural uranium/m^3 of air**, if its decay products are present in equilibrium, as in ore dust prior to chemical separation of the uranium from the ore

$U_{natural}$ (insoluble): 2.0E-11 µCi per ml (= 0.74 Bq/m^3, equiv. to **29,5 µg/m^3**)
(10 CFR 20, App. B, 1991)

U.S. Occupational Safety and Health Administration (OSHA) regulations

Permissible exposure limit ─ Time-weighted average:

soluble uranium: **0,05 mg/m^3**

insoluble uranium: **0,25 mg/m^3**

(29 CFR 1910 Subpart Z Table Z-1, 1997)

Ingestion: Current standards (WISE, 2003)

WHO provisional guideline for drinking-water quality:

9 µg of uranium per litre

This value is considered to be protective for subclinical renal effects reported in epidemiological studies. It is based on the assumption of a 60-kg adult consuming two litres of drinking water per day and a 50 per cent allocation of the TDI to drinking water. (WHO, 2003)

This value supersedes the earlier 2 µg/l provisional guideline, which was based on only 10 per cent allocation of the TDI to drinking water. (WHO, 1998).

(see also Issues)

Health Canada - Interim maximum acceptable concentration (IMAC) for uranium in drinking water:

20 µg per litre

(see also Issues)

U.S. EPA - Rule on radionuclides in drinking water:

Maximum contaminant level for naturally occurring uranium: **30 µg per litre**

EPA determines a safe level of 20 µg/L, assuming that an adult with a body mass of 70 kg drinks two litres of water per day and that 80 per cent of exposure to uranium is from water. For cost considerations, however, EPA established a standard of 30 µg/l rather than 20 µg/l. (65 FR 76707, 7 Dec. 2000)

(see also Issues)

U.S. EPA - Preliminary remediation goal (PRG) for Superfund:

2,22 µg per litre for U-238 in tap water

(see also Issues)

U.S. EPA - Groundwater standards for remedial actions at Iiactive uranium processing sites:

Maximum concentration limit for combined uranium-234 and uranium-238: **30 pCi/l** (1.11 Bq/l)

(Where secular equilibrium obtains, this criterion will be satisfied by a concentration of **0,044 mg per litre** (0,044 mg/l = 44 µg/l). For conditions of other than secular equilibrium, a corresponding value may be derived and applied, based on the measured site-specific ratio of the two isotopes of uranium.)

(40 CFR Part 192 (PDF-format); 60 FR 2854, 1995)

U.S. NRC Occupational Annual Limits on Intake (ALIs) for oral ingestion:

> $U_{natural}$: 10 µCi (= 14.,8 g)
>
> (10 CFR 20, Appendix B, 1991)

Australian Drinking-Water Guidelines:

> The concentration of uranium in drinking water should not exceed **0,02 mg/l** (= 20 µg/l)
>
> (ADWG, 1996, updated September 2001)

Australian Agricultural Water Standards for uranium:

The Australian Agricultural Irrigation Water Standards for uranium Desirable contamination concentration (DCC) of uranium in irrigation water is 0,01 mg/l, the Acceptable Contaminant Concentration (ACC) is 0,1 mg/l, and the soil Cumulative Contaminant Loading limit (CCL) has not yet been determined (ANZECC, 2000).

The Australian recommended water-quality guideline values (low risk) for uranium in livestock drinking water is 0,2 mg/L (ANZECC, 2000).

The Australian guideline concentrations for the upper limit of radiological contaminants in agricultural waters for irrigation and livestock drinking-water uses for uranium 238 is 0,2 Bq/L.

Trigger levels for uranium in fresh water were stipulated at 3,5 µg/L (ANZECC, 2000).

South African Water-Quality Guidelines

The maximal uranium concentration advised by the DWAF in water used for irrigation is 0,01 mg/l (DWAF, 2001:Water-quality guidelines. Irrigation. Tentative guideline for uranium. CD).

9.7.6 Summary of toxicity information

Susceptible populations

The susceptible population considered in this brief example of a risk assessment is the informal communities living next to the river.

Rags Table ─ Values used for daily intake calculation

Table 18: Table 4.1.RME - Values used for daily intake calculations ─ Reasonable maximum exposure

Exposure route	Receptor population	Receptor age	Exposure point	Parameter code	Parameter definition	Value	Units	Rationale/ reference	Intake equation/ model name
Water	Resident	Adult/ child	Drinking water	CW	Chemical concentration in water	See Table 3.1	mg/ l	See Table 3.1	Chronic daily intake (CDI) (mg/kg/day) =
				IR-W	Ingestion rate of water	2	l/day	EPA, 1991	CW x IR-W x EF x ED x 1/BW x 1/AT
				EF	Exposure frequency	350	days/year	EPA, 1991	= CW x 2,74E-2
				ED	Exposure duration	24	years	EPA, 1991	
				BW	Body weight	70	kg	EPA, 1991	
				AT-C	Averaging time ─ cancer	25,550	days	EPA, 1989a	
				AT-N	Averaging time ─ non-cancer	8,760	days	EPA, 198	

Rags Tables ─ Non-cancer toxicity data

Table 19: RAGS Table 5.1 ─ Non-cancer toxicity data ─ oral/dermal

Chemical of potential concern	Chronic/ subchronic	Oral RfD		Oral absorption efficiency for dermal	Absorbed RfD for dermal		Primary target organ(s)	Combined uncertainty/modifying factors	RfD: target organ(s)	
		Value	Units		Value	Units			Source(s)	Date(s)
Uranium	Chronic	0.6	µg/kg body weight/day	1	1.1	µg/kg body weight/day	Kidney	1 000	Wise	2003

Table 20: RAGS Table 5.1 - Non-cancer toxicity data ─ inhalation

Chemical of potential concern	Chronic/ sub-chronic	Inhala-tion RfC		Extrapolated RfD		Primary target organ(s)	Combined uncertainty/modifying factors	RfC : target organ(s)	
		Value	Units					Source(s)	Date(s)
Uranium	Chronic & subchronic	0.07	µg/m^3	4,55E-3	µg/kg/day	Lung	571	Wise	Jul 2003

Rags Table - Cancer toxicity data

Table 21: RAGS Table 6.1 ─ -Cancer toxicity data

Chemical of potential concern	Oral cancer slope factor (DDWC = Derived drinking water concentration)		Oral absorption efficiency for dermal	Absorbed cancer slope factor for dermal	
	Value	Units		Value	Units
Uranium-238	63	µg/L	1	63	µg/L

9.8 Risk characterisation ─ Summary, discussion and tabulation of the risk characterisation

Key site-related contaminants and key exposure pathways identified

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

Table 22 Rags Table ─ Risk summary

Medium	Exposure medium	Exposure point	Exposure route	Chemical of potential concern	EPC		Cancer risk calculations					Non-cancer hazard calculations				
					Value	Units	Intake/Exposure concentration		CSF/Unit risk		Cancer risk	Intake/Exposure concentration		RfD/RfC		Hazard quotient
							Value	Units	Value	Units		Value	Units	Value	Units	
Surface water	Surface water	Drinking water	Ingestion	Uranium	70	µg/L	140*	µg/L	63	µg/L	2,22**	4***	µg/kg/day	0.6	µg/kg/day	6,67
			Exp route total								2,22					6,67
		Exposure point total									2,22					6,67
	Exposure medium total										2,22					6,67
Surface water total											2,22					6,67

*see remarks on usage of this value in Table 13

** $\frac{140}{63} = 2{,}22$

*** Based on a 70 kg individual, drinking 2 litres of water per day: Total intake =280 µg, Exposure = 4 µg/kg/d, $\frac{4}{0{,}6} = 6{,}67$

Types of health risk of concern

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

Magnitude of the carcinogenic and non-carcinogenic risk estimates

The carcinogenic risk-quotient estimate for the surface water is 2,22, and the chemical-risk estimate for this water is 6,67.

Both risk quotients might be up to two orders of magnitude higher if maxima of uranium concentrations found in previous studies are considered. This ranges from a factor to be applied to the calculated risk quotient of 2,8 for water from the stream (based on 0,4 mg U238/l found in the upper Wonderfonteinspruit at C2H152) and a factor of >20 for drinking water from a mine canal (based on 3 mg U238/l found at Doornfontein process-water canal at C2H159) (both Carter, 1997) to a factor of 114 (times the calculated risk quotient) if the uranium concentration in Robinson Lake is considered (16 mg/l, Coetzee et al., 2003). The latter would be justifiable since the lake received contaminated groundwater originating largely in underground mine workings of the Wonderfonteinspruit catchment.

Major factors driving risk

Major factors driving risk are:

- contaminants mobilised from tailings dams, by metallurgical processes and underground mining activities entering the fluvial systems via base flow, run-off and point discharge of mining effluents; and

- the practice of drinking from the contaminated streams and mine-water canals in the catchment.

Major factors contributing to uncertainty

Amongst other factors, uncertainty results from the lack of understanding temporal dynamics of uranium concentrations in ground- and surface-water systems of the catchment, and in general which cause pronounced variations of the degree of water contamination according to flow rate, meteorological conditions, season, pumping rates and a number of natural processes such as photosynthesis that result in diurnal fluctuation of uranium concentrations. In addition, accumulative errors pertaining to analytical procedures and the suboptimal selection of best-suited sampling sites and methodology also contribute to uncertainty of the data used in this study.

Another group of factors contributing to uncertainty pertains to the area of probabilistic risk estimation based on epidemiological data. With many data for humans derived from short-term and high-dose exposure (e.g. from workforce at nuclear-power plants, etc.) and from animal experiments (especially regarding genetic implications), there is a general lack of data of impacts pertaining to low-dose and long-term exposure of humans to uranium and other contaminants. Furthermore, currently used factors to quantify health risk arising from radiation are largely based on generalised assumptions and do not reflect differences in the susceptibility of members in receiving populations and the organs affected, or synergetic effects resulting from combined exposure to chemical and radiological stress.

The risk model employed for the radiological risk quotient is based on assumptions regarding the total dose likely to be associated with water with a uranium concentration of 63 µg/l. As such, this is not a full radiological risk assessment, which would require nuclide specific data. The higher risk quotient calculated for chemical toxicity is independent of the uranium progeny, and therefore can be applied with certainty.

Exposed population characteristics

Exposed populations are expected to consist largely of residents in informal settlements with an impeded ability to cope with additional health risk, due to malnutrition and high rates of HIV/AIDS and the adverse effects on the immune system. No access or suboptimal access to health-care facilities, and other environmental factors contributing to health stress such as air pollution (including in-house heating and veld fires), as well as drug abuse, exacerbate the situation.

10 Conclusion and recommendations (H. Coetzee)

10.1 The impacts of mining as seen in analytical data

Compared with the global mean concentration of uranium in fresh water (discharge-unweighted) of 0,0004 mg/l (IWQS, 1999) the maximum concentration reported in stream water of the Wonderfonteinspruit is up to 1 000 times above natural background levels. Uranium maxima encountered in mine process water, and a lake affected by decanting groundwater from abandoned underground mine workings, are even higher, exceeding natural levels by four orders of magnitude. (factors 10 000 and 40 000 respectively).

A significant volume of analytical data on sediments from the Wonderfonteinspruit catchment has been collected during the course of this study. These data indicate concerning levels of contamination by a number of metals, with uranium and cadmium posing the greatest environmental hazard.

Sequential extractions performed on a set of samples, using an accepted standard experimental method,, confirm the results previously reported by Wade et al. (2002) and Coetzee et al. (2002) insofar as the contaminant metals are bound to a number of different phases within the sediment. It has been demonstrated that the processes binding the metals to the sediment are reversible and plausible changes in the local environment could remobilise a significant portion of these contaminants.

The largest fraction of contaminant metals is found in the reduced phase of the sediments, comprising organic material and sulphides. This poses a particular challenge, as allowing these sediments to become oxidised could release these metals. It is therefore important to ensure that the sediments are not allowed to dry out.

With specific regard to uranium, the uranium concentration at many of the sites sampled significantly exceeds the legislated exclusion limit for regulatory control. The National Nuclear Regulator must therefore be informed of the findings of this project and should investigate appropriate action.

10.2 Isotopic data

Two isotopic studies were undertaken as part of this study. Stable sulphur and strontium isotopes suggest a two-component mixing relationship between mine water and dolomitic groundwater. These two isotopic systems, along with some of the water chemistry, may be used to determine the relationship between these two sources in any water sample taken from the catchment.

Lead isotopes are particularly useful in tracking pollution from uranium-mining activities. Two lead isotopes — ^{206}Pb and ^{207}Pb — are derived from the decay of uranium. The combination of uranium concentration at the time of ore formation and the age of the ore deposit can produce widely varying lead-isotopic compositions which may be used to fingerprint the source of a contaminant stream.

The results recorded in this study show that lead isotopes are extremely useful on a local scale. The method demonstrated here does not necessarily have the resolution for unravelling complex regional-scale mixtures, except in areas where individual ore bodies have uranium concentrations significantly higher than others within a goldfield. For example, the lead-isotope study presented in this report was able to clearly fingerprint a highly radiogenic contribution to the lead contamination of sediments. This lead will undoubtedly come from a gold mine with a high uranium content in the ore. It would, however, be necessary to undertake a large-scale sampling and isotopic-analysis programme to be able to fingerprint individual mines' contribution to the contaminant stream in the Wonderfonteinspruit.

10.3 Temporal variations as determined using real-time continuous monitoring

The use of continuous real-time monitoring holds significant advantages for this type of pollution study. The range of values recorded can be used to constrain speciation and other geochemical models of the water in the system, while monitoring of individual natural and anthropogenic events allows the identification of possible mechanisms for the episodic transport of pollution.

Conventional sampling programmes, such as that undertaken by the Department of Water Affairs and Forestry for radionuclides (IWQS, 1999), must take the diurnal, as well as the seasonal, variations into account. For example, in the diurnal variations we see an increase in temperature and Eh, and a decrease in pH occurring at night, when most fissure water is discharged. These factors will combine to increase the solubility of uranium. All samples for the DWAF study were, however, collected during the day-time hours, some at approximately the same time of day on the same day of the week for each sampling point. It is therefore recommended that similar studies be implemented in any catchment-wide study of pollution.

An overview on the most important conclusions of this part of the study is presented in Section 8.6.

10.4 Risk assessment

A Tier-II risk assessment was performed, using templates from the USEPA Risk Assessment Guidance for Superfund (RAGS) as a guide for consistency and completeness.

In the exposure-assessment component of the risk assessment, sources, pathways to man, and mechanisms of transport and immobilisation were identified. In order to validate these mechanisms, a modeling strategy was considered. In preparation for the study an inventory of applicable modeling programmes was compiled, and the relative attributes of the packages compared. This included the application of chemical fate and transport modeling of uranium in the geosphere. In conclusion, the latest version of PHREEQC (Version 2.4.2) was identified as best-suited model to predict possible speciation of uranium in different aquatic environments and was therefore used in this study for the assessment of its environmental transport.

In the toxicity-assessment component of the risk assessment, published studies on toxic effects of uranium to man and other animals were studied. The two exposure routes of uranium (not concerning daughter products) of most importance to man are ingestion and particle inhalation.

Data for environmental processes were available only pertaining to the ingestion pathway, and thus a risk characterisation was performed on the scenario of humans drinking river water with the maximum measured concentrations of uranium.

The results of the risk characterisation are as follows: Chronic radiological (cancer) risk quotient = 2,22; Chronic chemical (nephrotoxicity) risk quotient = 6,67. An acceptable risk quotient is below 1,00. It should be borne in mind that the radiological risk quotient is calculated simply on the basis of the uranium concentration, determined by chemical analysis, and that radionuclide-specific analysis would provide a more precise result. Based on information determined during previous studies of the Wonderfonteinspruit, this approach should be regarded as highly conservative for the estimation of the radiological risk. The chemical toxicity quotient is, however, not dependent on the isotopic composition of the uranium in the water or on other radionuclides.

Thus, it was determined that the river water in some parts of the Wonderfonteinspruit catchment represents a hazard to residents who may ingest the water. It is, however, important to note that these areas have been identified and that warning signs have been put in place by local government. Furthermore, this hazard would only translate into a risk if people were to drink this water.

Since some of the sources of pollution are not due to direct discharge, but rather to run-off from contaminated sites and groundwater recharge, it can be expected that the hazard identified here will remain after the closure of mines. This implies a long-term responsibility to ensure that the hazard does not translate into a risk. It is also important to remember that some of the sites where these hazards exist are off mine property.

Monitoring of uranium concentrations at the inlet to the Potchefstroom waterworks has shown that this water does not currently represent a long-term risk due to radiation (IWQS, 1999). Grab sample results have at times however exceeded the levels identified in this study for the chemical toxicity of uranium (pers. comm. B Nel).

10.5 Medium- to long-term predictions

The current flow of the Wonderfonteinspruit is dominated by anthropogenic discharges, with mine fissure water playing a major role, particularly in the Lower Wonderfonteinspruit catchment. These inputs result in a relatively large perennial flow. The other major perennial input is the discharge of sewage-treatment works along the catchment. This input will not continue indefinitely. All mines have a finite life, and on closure the pumping of fissure water will cease. This has already happened in the upper Wonderfonteinspruit catchment.

Mine closure is expected to have the following effects:

1. Following mine closure the fissure-water input will immediately cease, considerably decreasing flow in the river. Input from sewage-treatment works will continue, although the population may be reduced as the local mining-based economy slows down. It is likely that portions of the river not fed by dolomitic springs will be returned to their premining non-perennial status. The lower portion of the river, which was historically fed by dolomitic springs, will probably undergo a dry period while the aquifer which has been dewatered recovers.

This low-flow regime will continue for a period of several years, possibly decades, during which time the reducing conditions currently found are likely to be compromised. If sediments are allowed to dry out, they could become a significant source of acid drainage by virtue of their sulphide content. The combination of oxidising and acidic conditions is ideal for the release of metals trapped in the sediment.

2. This phase will be followed by the groundwater-rebound phase, during which water levels will rise in the underground workings. This has already happened in the Krugersdorp–Randfontein area (Coetzee et al., 2003), where water has started to

    a. Decant from a number of shafts into the Tweelopiesspruit catchment immediately to the north of the Wonderfonteinspruit.

    b. Flow into the local dolomitic aquifer.

    This water has a low pH and a high acidity, owing to the elevated ferrous iron content in the decanting water. The water level is still rising in this area and may decant into the Wonderfonteinspruit. This inflow would have a serious impact on any contaminated sites downstream, as was seen in the initial decant, where acid mine water was discharged into Robinson Lake. The combination of pH- and redox-driven reactions resulted in a measured uranium concentration of 16 mg/l, and resulted in the NNR declaring the lake a radiation area.

    In the lower Wonderfonteinspruit catchment, three models exist as to the likelihood of such a decant occurring. Since the dolomitic eyes are below the levels of the shafts in each compartment, decant will happen at the eyes. Much has been speculated relying on the buffer capacity of dolomite; however, acid mine water can armour the dolomite with a ferric hydroxide gel if oxygen is present. This would limit the potential of the dolomite to neutralise the low pH in the long term.

    Whether this decant occurs only at Turffontein Eye or at all the eyes in the dewatered area, its impact is likely to be significant. Experience has, however, shown (pers. commun. P Younger) that the water quality in these decants of contaminated water tends to improve with time, although premining qualities are unlikely to be achieved.

3. Following the rebound and acid decant phases, infiltrating rainfall will determine the flow out of the dolomite, with the possibility of dry periods during winter and drought periods having been proposed in some models. During these periods wetland sediments may well be exposed to air, leading to acid production and the release of metals.

The current situation is therefore not sustainable in the longer term. Water and sediment analyses indicate that the heavy-metal contaminant stream does migrate downstream, and the likely impacts of the rewatering scenarios sketched here imply that sediments may become potential sources of contamination.

10.6 Methodological considerations

This study has been undertaken to answer the following questions:

1. What are the contaminants, where are they and how much is there?

   Using a combination of pre-existing data, semiquantitative analyses and quantitative analyses for confirmation, uranium and cadmium have been identified as major contaminants and a number of contaminated sites identified.

2. What processes cause the movement of contaminants from mining areas and their concentration in fluvial sediments? Can the contaminants be remobilised?

   Three major approaches have been used to answer these questions:

   - A conceptual model for uranium transport, grounded in environmental data, has been proposed.
   - Isotopic studies allow the characterisation of the water in the catchment, as well as the identification of pollution sources.
   - Speciation studies allow the identification of the processes binding pollution to sediments, as well as identifying possible remobilisation processes.

3. What are the temporal variations in river chemistry that have a bearing on the fate and transport of pollution?

   Frequent real-time monitoring of macrochemical parameters allows the identification of temporal variations within the catchment on a variety of scales. This information can be used to identify transport processes, as well as constraining chemical modeling.

   The monitoring data collected identified a number of points in the diurnal cycle that are not adequately sampled by a conventional sampling and analysis programme. To adequately capture these cycles, it is recommended that the temporal variability of water-quality parameters be understood before embarking upon expensive sampling programmes.

4. What about the end users? Direct analyses and long-term integration methods indicate possible pollution of downstream water resources. The assessment of risk identified the chemical toxicity of uranium as the primary risk factor and therefore did not follow the form of a radiological risk assessment.

5. Synthesis in the form of a risk assessment.

This methodology has been successfully applied to uranium contamination in the Wonderfonteinspruit catchment. It is, however, generic enough to be easily adapted to other contaminant or geographical settings.

10.7 Recommendations

1. 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.
2. 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.
3. 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.
4. 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.
5. 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.

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Appendix – Analytical data

Table 23. Semiquantitative ICP-MS scans for sediment samples collected on 23 May 2001 in the reconnaissance sampling programme (all values in µg/kg)

Sample	W1	W2	W3a	W3crust-a	W3crust-b	W3crust-c	W4	W4	W6	W7	W8	W8crust
Li	5277	9298	6954	8423	5056	3286	6531	12290	7438	8600	2503	2774
Be	967	1250	901	1278	723	1272	487	1957	429	818	251	993
B	0	0	0	0	0	0	0	0	0	0	0	0
Na	5859	128048	19333	662163	875244	484099	0	1670	65589	158258	83738	2665345
Mg	5697810	4237464	2768000	7300045	53254197	9381175	1901112	5175034	2140411	1791081	786571	4390390
Al	5083522	7696398	3757322	7043209	3990333	3748872	3044578	9840743	4331698	6668596	1980552	11432660
Si	2483	0	0	0	0	0	0	0	0	0	0	0
P	131976	243498	154043	114003	88795	51480	62444	331557	45975	69468	78029	41336
K	248213	647262	233749	1144712	525363	510832	219894	461567	353590	329186	186743	421980
Ca	2760666	5407599	2527058	7148595	4328687	5403366	1058786	941178	1743669	1785427	1007622	2308430
Sc	5776	11171	4565	5509	4214	2809	3111	11215	7364	8662	2263	14007
Ti	230777	423478	155275	209826	164081	104417	112363	386477	119225	271199	49060	422349
V	75502	131688	54783	63555	70128	58202	48904	85845	65764	124124	38340	207500
Cr	265547	226434	115810	132680	93970	245112	81972	117701	73756	351575	43160	777288
Mn	4487831	26747711	408357	2131682	11894873	3410179	203815	534989	468178	3318369	3010178	1320210
Fe	39584490	144647239	23885176	46911112	98658247	62265763	11739672	43217096	12271026	55761896	24827853	109188420
Co	698576	490519	288812	1949907	3590299	4713786	157624	371015	104793	17501	75204	26591
Ni	1221280	613373	518771	3882546	7063514	8644963	313913	1043335	192251	17609	64554	40622
Cu	85206	112195	134200	144360	62663	157317	45511	305232	38821	24941	31326	55221
Zn	1694416	1312440	3326680	31922171	27529842	83878420	1737106	4785174	711898	49211	257029	214163
Ga	4598	7986	3102	6041	2715	3988	2034	7854	3058	6482	1557	8974
Ge	144	194	120	315	231	514	87	217	90	76	57	97
As	40220	97814	45684	35705	55626	51748	39241	62184	36317	39261	64404	43658
Se	1038	2538	3161	5688	2598	9226	1192	4298	737	962	1242	809
Br	0	0	0	0	0	0	0	0	0	0	0	0
Rb	4679	9140	5561	13865	3693	6122	5756	13686	10508	11165	1671	8509

Sample	W1	W2	W3a	W3crust-a	W3crust-b	W3crust-c	W4	W4	W6	W7	W8	W8crust
Sr	22416	110916	20288	59166	28597	65888	8670	21129	10993	12313	4516	15831
Y	19035	25113	25003	193020	14892	161913	9387	60579	8880	7841	6222	7861
Zr	2041	2391	1737	2489	3279	2780	1730	2069	1676	2869	824	3944
Nb	431	843	298	430	357	289	199	682	213	525	183	733
Mo	1654	6573	2404	1828	1783	5487	1401	2408	833	1756	935	2988
Ru	22	19	12	49	74	97	10	21	9	9	3	6
Rh	9	10	11	30	20	49	9	19	4	4	5	4
Pd	155	118	217	890	283	1517	18	250	0	102	48	119
Ag	1902	729	1448	1589	2112	1248	1211	3117	1324	1199	253	118
Cd	1322	794	4470	16668	4013	9446	1187	2542	869	0	602	458
Sn	5136	1379	974	1296	283	438	534	2574	595	1337	630	1395
Sb	1609	2453	901	598	621	824	411	1273	424	567	488	732
Te	73	84	24	21	0	49	1	44	0	54	42	75
I	3526	3463	776	856	306	210	188	1902	369	1552	5682	1179
Cs	1102	2345	1748	1391	459	516	1238	2794	1327	1105	380	722
Ba	370802	1840998	56270	113707	55924	66666	24197	150315	61455	231043	35591	258207
La	51280	56697	44637	220333	14389	308513	14305	103658	14257	12740	5580	12629
Ce	160027	181616	122673	512505	40153	761451	44193	314130	48881	52069	19007	90306
Pr	19450	21786	17337	70385	5315	108402	6302	47030	6143	4971	2441	4225
Nd	60995	68179	54765	192982	17572	361408	20762	136393	19406	16020	8103	12946
Sm	8650	11226	9391	28570	2984	48170	3503	20805	3337	2768	1655	2197
Eu	2511	3052	2656	8711	820	13868	924	5650	857	678	365	549
Gd	8551	10670	9744	41722	3659	57419	3603	21539	3343	2745	1851	2252
Tb	988	1299	1277	5152	475	6406	467	2544	436	363	253	302
Dy	4470	6367	6610	27280	2607	30192	2359	13032	2338	1888	1476	1690
Ho	641	933	958	4264	422	4199	346	1830	354	297	223	261
Er	1589	2482	2482	10133	1176	9345	894	4642	885	809	616	691
Tm	204	329	311	1104	146	997	118	593	117	110	87	100
Yb	1332	2149	1925	5880	988	5746	741	3770	796	771	567	710
Lu	160	284	226	716	120	665	89	435	93	101	71	90

Sample	W1	W2	W3a	W3crust-a	W3crust-b	W3crust-c	W4	W4	W6	W7	W8	W8crust
Hf	72	89	121	189	82	192	71	128	50	102	33	64
Ta	7	11	8	27	3	31	3	17	2	3	3	3
W	1929	1049	645	509	459	281	243	989	209	235	110	227
Re	1	4	6	9	9	6	2	3	1	0	0	1
Os	12	2	1	2	0	2	1	1	0	0	0	0
Ir	18	1	2	1	0	2	1	1	0	1	0	1
Pt	0	2	0	0	11	0	0	3	0	0	0	0
Au	6433	3561	3208	1530	503	336	1599	5916	975	51	569	59
Hg	477	413	244	168	265	71	236	608	172	91	213	60
Tl	283	808	161	340	132	267	96	296	100	226	72	201
Pb	96222	38016	29480	17858	10983	11168	13027	53475	14243	30397	20985	43247
Bi	502	624	506	490	597	405	410	926	435	518	1481	427
Th	381	473	496	348	155	143	305	846	440	361	557	473
U	215305	334249	644784	348715	185154	181276	218269	925168	109715	12366	57020	32562

Table 24. Semiquantitative ICP-MS scans of sediment samples collected on 15 August 2001 in the reconnaissance sampling programme (all values in µg/kg)

Sample	W101	W101	W102	W102	W102	W103	W103	W105	W106	W107	W107	W108	W109
Li	25931	11952	11905	9487	11191	23224	9346	6758	9793	22495	4665	3013	3168
Be	1768	1290	759	669	1076	843	308	460	671	1795	423	250	472
B	0	1193	3160	2121	2402	2501	1466	2378	2441	2052	704	355	265
Na	174322	185565	604322	177246	25264981	1242303	99284619	153708	239951	274084	191330	276259	145162
Mg	571584	666196	1002303	519424	9243996	2355949	52088770	880464	631844	4379514	641904	249992	721729
Al	7054633	5185819	6727417	4455040	15210780	5180336	5488718	4859277	12338670	15348604	3206279	4055443	4997585
Si	539243	547308	466724	439336	1090387	297857	569511	270377	353183	433807	256975	228550	256785
P	115923	163732	185793	194779	215496	141787	87099	93032	402837	367402	66999	575910	70283
K	1075383	511427	1340433	525540	2549897	797555	1812433	1788437	988791	1504533	449810	445342	377541
Ca	2600647	8610321	4619759	3456166	13386941	9672804	7383602	5352808	2904106	3477614	6615131	1055773	828981
Sc	6214	5045	3651	2800	6209	3175	1633	2082	8264	6329	2113	1864	3569
Ti	324665	281744	270135	193091	880788	192762	185978	163982	446955	245634	129175	79275	172815
V	177685	157566	115551	104448	214625	113155	130734	79524	134690	109293	70985	65789	87574
Cr	484028	410339	326301	297280	348835	255856	146643	267205	216152	272179	239447	189497	323186
Mn		24953366	16267498	12770805	26141512	16129376	4483375	5377510	2048360	5739261	2943945	369999	2343346
Fe	87028177	84016097	49093925	49720651	70804831	32867733	14231516	20335627	54076976	43332834	13115782	17810234	38628838
Co	74058	56456	35692	34836	54039	39476	12806	15314	27459	506151	13617	12027	36465
Ni	226095	154448	110230	151642	145339	162732	85391	158232	114979	1852372	48850	69146	160781
Cu	75667	57671	35202	38827	42811	47872	24951	23575	33338	152199	16840	24967	67978
Zn	33244	24545	47451	49156	51438	28480	31691	34065	70686	993513	13646	47422	112948
Ga	9286	6353	5475	4209	8817	4387	2405	2918	7771	7720	2368	2452	3884
Ge	340	294	193	187	318	230	253	160	215	379	106	132	181
As	45640	45226	34242	36661	68215	34392	59413	27855	32241	88495	26290	30302	40838
Se	755	888	636	934	1360	545	992	425	997	2316	664	522	925
Br	0	7964	24421	15370	20450	20146	15260	5144	32489	14006	17887	17309	0
Rb	5058	3331	8256	4332	12137	6127	5761	12175	15523	11675	5908	3601	2580
Sr	46390	30460	32718	27883	115139	18778	15903	7176	14624	18559	7140	4659	6791

Sample	W101	W101	W102	W102	W102	W103	W103	W105	W106	W107	W107	W108	W109
Y	12970	10684	6562	5598	7549	5221	2078	3640	10032	31354	3178	4268	9652
Zr	8333	4734	3206	2707	7962	3006	4652	2460	3654	2835	2329	1544	3547
Nb	742	700	568	446	801	422	265	324	982	619	281	196	286
Mo	6527	3825	4626	3522	6978	4091	3330	1695	2628	3327	1439	1717	2221
Ru	18	19	11	10	11	10	5	8	9	25	4	6	11
Rh	19	10	9	8	15	9	4	5	7	14	4	4	6
Pd	560	378	144	142	322	134	243	134	172	409	125	119	137
Ag	224	193	84	84	285	128	50	52	97	377	63	174	69
Cd	0	91	0	0	163	107	188	0	9	2008	0	0	242
Sn	404	251	763	969	1252	381	642	463	1271	6149	412	506	392
Sb	962	806	581	727	788	532	272	253	811	1439	219	171	517
Te	54	45	38	24	31	10	0	10	61	65	0	249	42
I	946	470	651	260	1152	476	424	358	566	1725	597	369	348
Cs	594	449	747	710	800	435	284	1167	1874	3626	542	569	524
Ba	4147894	2533252	1728593	1492568	2814549	1592917	466648	186749	190909	155620	265603	59139	140951
La	40172	26355	13266	11582	16059	14330	4535	9591	15078	67163	6892	6433	10140
Ce	155176	105296	50527	43092	64574	71040	17880	27204	41086	145497	24197	14583	39000
Pr	9107	6519	3438	2852	3908	3427	1164	2437	4282	16729	1731	1931	4197
Nd	25091	18769	9655	8219	11399	9588	3402	7035	13176	50932	5011	5990	13426
Sm	3814	2833	1468	1256	1680	1456	601	1048	2123	7554	779	930	2130
Eu	1169	810	466	389	653	457	158	223	468	1950	190	212	506
Gd	2900	2173	1180	1055	1392	1124	453	822	1789	6641	645	806	1966
Tb	355	275	144	125	168	149	51	99	208	759	77	99	217
Dy	2032	1513	853	709	959	811	298	518	1260	4160	447	549	1221
Ho	333	246	145	122	158	134	48	85	213	657	73	93	200
Er	960	713	410	356	464	371	127	243	623	1718	224	257	543
Tm	148	113	62	53	71	58	20	39	91	226	34	37	78
Yb	1135	863	469	413	571	436	163	262	696	1648	254	265	546
Lu	166	124	70	59	86	71	23	36	88	187	34	34	70
Hf	109	62	64	46	113	63	84	44	69	82	54	32	57

Sample	W101	W101	W102	W102	W102	W103	W103	W105	W106	W107	W107	W108	W109
Ta	8	8	4	3	6	3	1	2	4	9	1	1	3
W	2176	1447	2947	1510	230	2579	82	1985	769	3078	2135	3520	2730
Re	2	2	1	1	4	2	13	0	0	1	1	0	0
Os	1	1	1	0	1	1	0	0	0	1	0	0	0
Ir	12	14	10	20	24	11	22	11	10	9	13	11	11
Pt	50	53	50	96	103	51	88	43	47	50	51	50	47
Au	37	147	159	360	34	36	12	1	299	1545	57	58	46
Hg	32	9	59	4	68	77	128	54	398	261	86	88	72
Tl	1394	859	485	399	722	672	183	186	211	148	207	50	77
Pb	43436	28269	21993	19423	30606	32564	12012	16327	19288	112304	11567	9276	14781
Bi	95	72	82	53	85	82	29	54	202	659	57	126	204
Th	25511	17873	12919	12428	23883	11952	6991	15473	34629	52919	11263	12748	14956
U	49547	66375	107690	248125	178947	0	0	0	542149	578213	0	32541	245143

Table 25. Concentrations and tier-1 risk quotients (depicted with shading) for selected metals from the reconnaissance sampling programme (all concentrations in mg/kg)

	Cr	Co	Ni	Cu	**Zn**	**As**	**Cd**	**Pb**	**Th**	**U**
Reference value	*65*	*20*	*35*	*36*	*4500*	*19*	*0.001*	*85*	*50*	*16*
Source	*EU*	*EU*	*EU*	*EU*	*EU*	*EU*	*EU*	*EU*	*NNR*	*NNR*
W1	**265.55**	**698.58**	**1221.28**	**85.21**	1694.42	**40.22**	**1.32**	96.22	0.38	**215.31**
W2	**226.43**	**490.52**	**613.37**	**112.20**	1312.44	**97.81**	**0.79**	38.02	0.47	**334.25**
W3a	115.81	**288.81**	**518.77**	**134.20**	3326.68	**45.68**	**4.47**	29.48	0.50	**644.78**
W3crust	**132.68**	**1949.91**	**3882.55**	**144.36**	**31922.17**	35.71	**16.67**	17.86	0.35	**348.72**
W3crust	93.97	**3590.30**	**7063.51**	62.66	**27529.84**	**55.63**	**4.01**	10.98	0.16	**185.15**
W3crust	**245.11**	**4713.79**	**8644.96**	**157.32**	**83878.42**	**51.75**	**9.45**	11.17	0.14	**181.28**
W4	81.97	**157.62**	**313.91**	45.51	1737.11	**39.24**	**1.19**	13.03	0.31	**218.27**
W4	117.70	**371.02**	**1043.34**	**305.23**	4785.17	**62.18**	**2.54**	53.48	0.85	**925.17**
W6	73.76	**104.79**	**192.25**	38.82	711.90	36.32	**0.87**	14.24	0.44	**109.72**
W7	**351.58**	17.50	17.61	24.94	49.21	**39.26**	0.00	30.40	0.36	12.37
W8	43.16	**75.20**	64.55	31.33	257.03	**64.40**	**0.60**	20.99	0.56	**57.02**
W8	**777.29**	26.59	40.62	55.22	214.16	**43.66**	**0.46**	43.25	0.47	**32.56**
W101	**484.03**	**74.06**	**226.10**	**75.67**	33.24	**45.64**	0.00	43.44	25.51	**49.55**
W101	**410.34**	**56.46**	**154.45**	57.67	24.55	**45.23**	**0.09**	28.27	17.87	**66.38**
W102	**326.30**	35.69	**110.23**	35.20	47.45	34.24	0.00	21.99	12.92	**107.69**
W102	**297.28**	34.84	**151.64**	38.83	49.16	36.66	0.00	19.42	12.43	**248.13**
W102	**348.84**	**54.04**	**145.34**	42.81	51.44	**68.22**	**0.16**	30.61	23.88	**178.95**
W103	**255.86**	39.48	**162.73**	47.87	28.48	34.39	**0.11**	32.56	11.95	0.00
W103	**146.64**	12.81	**85.39**	24.95	31.69	**59.41**	**0.19**	12.01	6.99	0.00
W105	**267.21**	15.31	**158.23**	23.58	34.07	27.86	0.00	16.33	15.47	0.00
W106	**216.15**	27.46	**114.98**	33.34	70.69	32.24	**0.01**	19.29	34.63	**542.15**
W107	**272.18**	**506.15**	**1852.37**	**152.20**	993.51	**88.50**	**2.01**	112.30	52.92	**578.21**
W107	**239.45**	13.62	48.85	16.84	13.65	26.29	0.00	11.57	11.26	0.00
W108	**189.50**	12.03	69.15	24.97	47.42	30.30	0.00	9.28	12.75	**32.54**
W109	**323.19**	36.47	**160.78**	67.98	112.95	**40.84**	**0.24**	14.78	14.96	**245.14**

□	< ½ Limit
▨	½ Limit → 2* Limit
■	> 2* Limit

Table 26. XRF results for a set of thirteen sediment samples collected in August 2003

Sample	**GN029**	**GN030**	**GN031**	**GN032**	**GN033**	**GN038**	**GN039**	**GN041**	**GN042**	**GN043**	**GN044**	**GN045**
Major Elements (%)												
SiO_2	52.01	81.71	64.68	59.88	54.81	53.79	55.50	51.34	81.39	83.43	83.51	54.80
TiO_2	0.41	0.34	0.38	0.25	0.45	0.30	0.67	0.51	0.56	0.39	0.41	0.30
Al_2O_3	9.59	3.84	7.02	4.82	12.76	17.43	11.25	9.60	8.64	5.89	7.21	7.32
Fe_2O_3(t)	8.12	2.86	12.92	15.71	8.46	10.60	2.83	5.82	2.06	2.80	2.12	13.94
MnO	1.11	0.33	0.31	1.98	0.12	0.14	0.04	0.22	0.02	0.11	0.04	2.29
MgO	2.56	0.21	0.22	0.24	0.44	4.73	1.27	2.29	0.29	0.27	0.26	0.34
CaO	3.78	1.53	0.83	1.18	0.62	0.53	8.72	2.44	0.33	0.36	0.38	2.43
Na_2O	1.03	0.31	0.16	0.18	0.33	0.23	0.32	0.64	0.20	0.28	0.15	0.13
K_2O	0.52	0.28	0.32	0.25	0.62	2.26	0.63	0.84	0.55	0.45	0.46	0.48
P_2O_5	0.10	0.37	0.35	0.22	1.90	0.09	0.31	0.18	0.11	0.22	0.12	0.17
Cr_2O_3	0.17	0.03	0.08	0.07	0.10	0.15	0.15	0.04	0.03	0.02	0.03	0.04
L.O.I.	20.44	8.29	13.07	14.98	19.56	8.88	18.07	26.08	6.37	5.61	6.05	17.44
TOTAL	99.84	100.10	100.33	99.76	100.18	99.14	99.77	99.98	100.54	99.84	100.72	99.67
H_2O-	1.64	0.41	0.30	0.70	0.61	0.42	1.19	0.75	0.37	0.40	0.47	0.76
Trace Elements (mg/kg)												
As	<10	<10	<10	<10	209	136	<10	<10	<10	<10	<10	<10
Ba	177	103	382	365	477	286	159	221	113	130	114	1681
Ce	187	71	65	90	321	116	50	28	44	90	22	127
Co	1126	149	47	176	188	349	37	24	30	239	26	109
Cr	909	147	555	480	617	934	916	216	166	118	145	315
Cu	303	18	53	55	466	292	52	42	37	68	20	54
Ga	9	<5	9	7	11	17	15	13	11	7	10	11

Sample	**GN029**	**GN030**	**GN031**	**GN032**	**GN033**	**GN038**	**GN039**	**GN041**	**GN042**	**GN043**	**GN044**	**GN045**
Hf	<5	11	6	<5	<5	<5	11	8	9	<5	8	6
Mo	4	<2	<2	3	5	3	<2	<2	<2	<2	<2	3
Nb	5	6	6	5	8	5	11	7	10	7	8	5
Ni	611	261	88	154	689	1138	72	72	138	698	78	172
Pb	28	8	18	29	327	436	11	<5	14	21	14	21
Rb	24	16	22	12	31	43	44	47	54	34	42	27
Sc	12	6	11	7	16	16	18	17	13	8	9	14
Sr	125	23	19	28	66	31	47	35	19	20	14	66
Ta	<5	<5	<5	<5	<5	8	<5	<5	<5	<5	<5	<5
Th	<5	<5	<5	<5	56	27	6	<5	8	6	5	<5
U	163	7	<3	21	439	264	40	<3	70	77	14	23
V	83	35	149	115	79	90	211	101	69	51	50	145
W	101	90	108	405	117	60	111	36	18	38	55	70
Y	40	24	13	12	99	46	53	15	18	23	13	17
Zn	499	211	125	159	957	646	33	62	105	1144	36	120
Zr	154	280	154	117	181	186	204	164	208	184	175	100

Table 27 Results of isotope analyses on water samples

Sample	**Description**	$\delta^{34}S$‰ CDT	**$^{87}Sr/^{86}Sr$**	$\delta^{87}Sr$‰ NBS987
		$SO_4$2-	Water	
HG01	Andries Coetzee's Dam	3,4	0,73106	**29,3**
HG02	Wonderfonteinspruit at Welverdiend	5,1	0,72951	**27,1**
HG03	Khutsong Bridge	4,6	0,73072	**28,8**
HG04	Donaldson Dam	13,6	0,72297	**17,9**
HG05	River at Donaldson Dam	11,2	0,72293	**17,8**
HG06	Weir (C2H069)	3,6	0,73314	**32,2**
HG07	Canal from Doornfontein (C2H060)	3,2	0,73543	**35,5**

Table 28. Results of S-isotope aliquot determinations on water samples from the Wonderfonteinspruit

Sample	Description	Mineral	Analysis	Sample weight [mg]	V_2O_5 weight [mg]	Total beam		**δ^{34}S‰ CDT**
HG01	Andries Coetzee's Dam	$BaSO_4$	D4	0,36	0,57	1,62E-07		3,422
			D5	0,40	0,70	1,95E-07		3,434
							avg.:	**3,428**
							diff.:	*0,013*
HG02	Wonderfonteinspruit at Welverdiend	$BaSO_4$	D6	0,38	0,65	2,68E-07		4,687
			D7	0,37	0,70	3,55E-07		5,498
							avg.:	**5,093**
							diff.:	*0,811*
HG03	Khutsong Bridge	$BaSO_4$	D8	0,36	0,81	2,24E-07		4,387
			D9	0,37	0,73	2,79E-07		4,870
							avg.:	**4,629**
							diff.:	*0,483*
HG04	Donaldson Dam	$BaSO_4$	D12	0,36	0,86	1,79E-07		13,527
			E1	0,36	0,62	2,13E-07		13,719
							avg.:	**13,623**
							diff.:	*0,192*
HG05	River at Donaldson Dam	$BaSO_4$	E2	0,37	0,72	1,76E-07		11,276
			E3	0,38	1,11	1,73E-07		11,054
							avg.:	**11,165**
							diff.:	*0,222*
HG06	Weir (C2H069)	$BaSO_4$	E4	0,45	0,75	2,57E-07		4,066
			E5	0,39	0,68	1,71E-07		3,214
							avg.:	**3,640**
							diff.:	*0,851*
HG07	Canal from Doornfontein (C2H060)	$BaSO_4$	E9	0,41	1,19	1,92E-07		3,444
			E10	0,37	0,78	1,67E-07		3,041
							avg.:	**3,243**
							diff.:	*0,403*

Table 29. Anion concentrations in water in mg/l

Sample	**F**	**Cl**	**NO_2**	**Br**	**NO_3**	**PO_4**	**SO_4**
Andries Coetzee's Dam	0	102	0	0	2	1	197
Wonderfontein-spruit at Welverdiend	0	100	0	0	2	2	187
Khutsong Bridge	0	100	0	0	1	0	192
Donaldson Dam	0	58	0	0	0	0	233
River at Donaldson Dam	0	65	0	0	1	0	290
Weir (C2H069)	0	99	0	0	4	1	329
Canal from Doornfontein (C2H060)	0	114	1	0	11	1	720

Table 30. Elemental concentrations in water samples in μg/l

Sample	**Li**	**Be**	**B**	**C**	**Na**	**Mg**	**Al**	**Si**	**P**	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**
Andries Coetzee’s Dam	13	0	91	68213	70473	37430	66	1185	264	7083	59795	1	2	8	18	6	92	10
Wonderfonteinspruit at Welverdiend	13	0	81	76234	65568	36211	52	1468	509	7041	59809	1	4	6	19	49	56	8
Khutsong Bridge	18	0	67	73873	68320	38899	57	1551	147	6091	64373	1	3	6	89	9	297	10
Donaldson Dam	12	0	43	73326	64458	23714	118	474	16	12204	82097	0	3	3	133	191	634	6
River at Donaldson Dam	9	0	48	81247	67696	26977	56	1598	73	10677	96370	1	1	1	27	316	158	10
Weir (C2H069)	19	0	70	66392	74928	44696	60	1530	242	7066	75073	1	3	7	62	67	231	23
Canal from Doornfontein (C2H060)	33	0	91	14081	108909	78693	126	2227	151	6378	128976	2	2	2	43	135	181	101

Sample	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Ru**	**Rh**	**Pd**	**Ag**
Andries Coetzee’s Dam	70	4	32	0	0	8	4	633	10	206	0	2	0	4	0	0	0	0
Wonderfonteinspruit at Welverdiend	36	2	48	0	0	9	3	602	10	205	0	2	0	3	0	0	0	0
Khutsong Bridge	88	6	57	0	0	10	4	646	9	211	0	2	0	4	0	0	0	0
Donaldson Dam	104	6	38	0	0	3	4	470	17	168	0	1	0	2	0	0	0	0
River at Donaldson Dam	34	5	99	0	0	3	3	468	17	187	0	2	0	1	0	0	0	0
Weir (C2H069)	225	4	49	0	0	7	5	588	10	288	0	1	0	4	0	0	0	0
Canal from Doornfontein (C2H060)	611	6	50	0	0	4	5	649	11	619	0	2	0	4	0	0	0	0

Sample	**Cd**	**Sn**	**Sb**	**Te**	**I**	**Cs**	**Ba**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**
Andries Coetzee’s Dam	0	4	1	0	0	0	18	0	0	0	0	0	0	0	0	0	0	0
Wonderfonteinspruit at Welverdiend	0	4	1	0	0	0	26	0	0	0	0	0	0	0	0	0	0	0
Khutsong Bridge	0	4	1	0	0	1	30	0	0	0	0	0	0	0	0	0	0	0
Donaldson Dam	0	6	0	0	2	0	54	0	1	0	0	0	0	0	0	0	0	0
River at Donaldson Dam	0	5	0	0	1	1	11	0	0	0	0	0	0	0	0	0	0	0
Weir (C2H069)	0	4	1	0	0	1	25	0	0	0	0	0	0	0	0	0	0	0
Canal from Doornfontein (C2H060)	0	5	1	0	1	2	33	1	3	0	1	0	0	0	0	0	0	0

Sample	**Tm**	**Yb**	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Th**	**U**
Andries Coetzee’s Dam	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	258219
Wonderfonteinspruit at Welverdiend	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	172997
Khutsong Bridge	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	242731
Donaldson Dam	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	110886
River at Donaldson Dam	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	252125
Weir (C2H069)	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	198729
Canal from Doornfontein (C2H060)	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	218678

Table 31 Quantitative ICP-MS analyses for sequential extraction study (all results in µg/l)

Extraction	Samples	Ni (60)	Cu (63)	Zn (68)	As (75)	Cd (111)	Hg (202)	Pb (208)	U (238)
A – Weakly Acidic	**029 A**	1013	393	2913	8	3	< 1	65	243
	030 A	770	39	1353	12	3	< 1	48	4
	031 A	77	209	683	10	1	< 1	56	0
	032 A	485	26	1817	10	2	< 1	135	14
	033 A	1311	243	3940	142	4	< 1	106	150
	038 A	2450	910	2708	17	9	< 1	291	608
	039 A	105	62	695	6	1	< 1	80	158
	041 A	38	21	753	5	1	< 1	71	0
	042 A	653	61	893	10	1	< 1	47	71
	043 A	3082	29	4025	26	2	< 1	50	28
	044 A	293	34	671	18	4	< 1	113	8
	045 A	193	27	829	3	4	< 1	35	11
	046 A	10382	480	6675	25	12	< 1	83	606
	Blank A	6	28	614	13	1	< 1	74	0
B – Weakly Reducing	**029 B**	2735	475	2726	22	2	< 1	90	233
	030 B	1241	27	2010	31	2	< 1	112	3
	031 B	114	39	985	23	4	< 1	125	1
	032 B	238	23	735	37	3	< 1	94	11
	033 B	917	286	1970	249	4	< 1	211	242
	038 B	908	821	1026	40	3	< 1	353	284
	039 B	77	8	359	18	1	< 1	39	7
	041 B	51	253	673	16	1	< 1	76	0
	042 B	607	87	1233	35	3	< 1	125	129
	043 B	1859	56	4942	35	4	< 1	65	43
	044 B	187	10	501	25	2	< 1	71	14
	045 B	209	26	2068	25	8	< 1	139	8
	046 B	1378	323	1309	47	3	< 1	125	205
	Blank	15	9	358	16	1	< 1	83	0
C – Weakly Oxidising	**029 C**	1373	1439	1839	42	3	< 1	106	537
	030 C	1921	142	2252	118	6	< 1	102	40
	031 C	215	233	904	26	3	< 1	97	12
	032 C	125	101	618	56	2	< 1	164	47
	033 C	1939	1539	1667	747	6	< 1	234	901
	038 C	3035	2822	2214	129	5	< 1	89	958
	039 C	233	232	842	30	1	< 1	70	175
	041 C	123	179	555	35	1	< 1	98	9
	042 C	512	234	793	85	1	< 1	46	413
	043 C	1710	415	3858	105	4	< 1	84	196
	044 C	420	115	483	57	1	< 1	90	91
	045 C	556	202	1530	46	3	< 1	92	55
	046 C	783	297	2075	344	5	< 1	186	86
	Blank C	32	18	590	13	1	< 1	35	0

Table 32 Semiquantitative ICP-MS analyses for sequential extraction study (all results in μg/l)

Sample	Li	Be	B	Na	Mg	Al	Si	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
029 A	22	6	218	90814	211790	11940	5391	0	13997	277789	6	25	3	191	13645	1087	982	868	338	2586
030 A	10	2	86	8227	7297	1770	2300	246	3265	229265	1	23	1	25	12441	371	333	744	36	1224
031 A	3	0	0	4419	4189	1679	999	271	3070	46199	0	8	19	37	11438	16782	74	79	178	606
032 A	4	0	46	5715	3172	1871	978	216	1869	32758	0	33	0	555	59306	1325	214	479	26	1666
033 A	21	5	1	6542	1806	10492	656	297	1930	21589	0	29	9	119	3786	7130	352	1165	227	3675
038 A	38	6	259	3520	8276	9180	2747	74	6538	299875	0	26	0	353	3694	4951	924	2309	870	2526
039 A	17	1	19	7637	26720	10516	5361	30	791	733380	10	41	73	1031	1943	3789	16	70	62	633
041 A	2	0	66	31571	93286	1547	3527	38	8654	107211	2	39	2	39	7508	785	26	31	22	679
042 A	18	2	4	4053	8164	1341	1177	48	2011	28783	0	14	34	34	800	2028	89	631	60	804
043 A	12	2	120	3797	5460	2350	1494	604	1467	18356	0	18	30	52	6777	25342	728	2805	28	3833
044 A	13	4	55	5425	6388	1712	1025	590	2787	29066	0	35	38	31	2487	20324	28	262	33	603
045 A	8	0	0	4959	5839	1385	821	27	2448	202246	0	45	0	0	18308	641	74	169	26	768
046 A	65	6	237	289061	1792805	11382	2405	0	26908	153861	0	28	0	138	22887	3226	1123	9516	442	6244
Blank A	2	0	476	2803	110	1146	127	0	372	243	0	6	0	55	14	304	0	2	29	545
029 B	47	5	156	7701	20416	21509	3782	0	2123	263949	0	20	56	99	74288	45168	4506	2571	452	2549
030 B	8	4	24	3163	2225	6942	2279	711	1447	85314	0	683	47	54	24519	21212	937	1202	26	1864
031 B	4	0	47	3500	1284	9160	925	308	1850	16849	0	25	75	26	13093	27462	114	106	38	804
032 B	6	0	4	2429	581	2634	514	364	804	4370	0	27	55	14	29907	28043	232	199	22	616
033 B	16	10	196	2398	507	33102	959	4691	642	4429	0	72	78	141	918	30326	166	907	274	1922
038 B	27	5	98	1592	4639	12125	3004	0	2376	133154	0	19	42	237	2222	24350	593	829	723	939
039 B	13	4	142	2660	11884	27941	6922	54	621	137641	0	24	741	508	528	12855	10	65	9	341
041 B	2	0	192	5734	36291	3230	3644	19	2170	64669	0	19	90	29	7166	27362	53	45	236	577
042 B	15	3	57	2727	1962	6444	997	247	1312	9865	0	47	243	61	351	25999	77	572	82	1128
043 B	8	3	475	3847	1340	6296	830	446	744	4353	0	21	84	40	2146	14864	384	1798	55	4571
044 B	9	3	15	2536	2024	3795	1044	142	1094	9574	0	49	95	31	892	14530	19	184	12	448
045 B	15	0	17	6387	1855	4064	826	172	2139	47249	0	34	73	374	55461	16008	232	196	26	1722
046 B	52	4	445	12175	72719	12940	1387	0	1765	236376	0	26	39	184	20642	17683	823	1262	292	1227
Blank	3	1	143	2098	227	712	0	0	398	306	0	11	35	59	19	319	0	11	10	323
029 C	49	3	246	13612	8625	29698	29592	3053	96	97594	199	300	84	3100	5419	28980	664	1242	1340	1775

Sample	**Li**	**Be**	**B**	**Na**	**Mg**	**Al**	**Si**	**P**	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
030 C	36	8	100	12563	1542	22576	28700	6792	408	57952	204	210	39	2764	4416	17670	567	1727	128	2076
031 C	42	2	112	18572	1034	28699	26994	6460	704	39747	175	234	208	3225	4067	8518	73	187	215	758
032 C	13	0	76	21899	672	5448	20933	10972	0	44339	188	275	39	2741	1921	2894	54	106	96	557
033 C	34	13	498	13718	848	40364	24769	11005	0	38603	168	214	73	3136	359	11437	303	1787	1377	1499
038 C	52	11	142	18044	5924	33406	28189	2371	796	84624	150	109	29	3578	1277	21579	592	2617	2514	1987
039 C	39	12	124	14288	15436	105672	35016	4518	808	111057	269	599	1014	6766	494	14227	23	197	210	696
041 C	19	1	629	15651	16663	26466	33900	7859	859	38120	197	1003	275	3275	1902	39448	52	90	170	463
042 C	105	2	480	13346	831	20993	29039	7964	478	43286	186	364	233	3414	96	9331	86	456	217	704
043 C	62	2	114	14817	1316	14602	25666	11046	328	33055	160	380	68	2972	427	4676	760	1605	399	3735
044 C	104	2	106	16523	799	20154	32449	10706	303	37166	207	342	117	3311	170	4941	97	379	114	417
045 C	39	6	134	13793	1386	15320	26908	6279	3004	48641	189	656	200	2966	143226	8544	375	494	184	1288
046 C	8	1	96	12466	5429	8035	25730	6593	0	99410	182	190	4	3824	580	3884	51	716	281	1940
Blank C	1	0	530	13500	278	1198	20091	13552	0	24910	182	175	0	2026	19	151	1	19	17	499

Sample	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ru	Rh	Pd	Ag	Cd	Sn	Sb	Te	I	Cs
029 A	3	1	8	12	308	22	1282	73	13	0	0	0	0	0	0	0	0	0	0	1	0
030 A	1	0	10	2	0	7	310	11	3	0	0	0	0	0	0	3	0	0	0	0	0
031 A	1	0	11	1	0	13	132	1	3	0	0	0	0	0	0	0	1	0	0	0	0
032 A	3	0	12	3	0	7	156	3	11	0	0	0	0	0	0	2	0	0	0	0	0
033 A	2	0	136	6	0	6	105	59	3	0	0	0	0	0	1	4	0	0	0	0	0
038 A	4	1	15	11	0	30	73	97	8	0	0	0	0	0	2	8	1	0	0	0	1
039 A	1	0	7	19	0	5	354	107	6	0	0	0	0	0	0	1	1	1	0	0	0
041 A	0	0	6	1	33	22	199	1	8	0	0	0	0	0	0	1	1	0	0	1	0
042 A	0	0	11	0	0	7	178	6	4	0	0	0	0	0	0	0	0	0	0	0	0
043 A	1	0	24	6	0	6	123	12	3	0	0	0	0	0	1	1	0	1	0	0	1
044 A	0	0	19	0	0	10	133	2	8	0	0	0	0	0	0	3	1	0	0	0	1
045 A	1	0	3	3	0	7	207	3	3	0	0	0	0	0	0	0	0	0	0	1	0
046 A	4	1	23	24	448	38	862	130	13	0	0	0	0	0	0	11	0	0	0	1	2
Blank A	0	0	13	3	0	0	22	0	4	0	0	0	0	0	24	1	0	1	0	0	0
029 B	8	1	17	9	158	15	1131	105	4	0	0	0	0	0	0	2	0	0	0	4	1
030 B	3	0	24	5	187	8	162	47	5	0	0	0	1	0	0	2	0	0	0	1	0
031 B	1	0	17	1	190	20	90	8	6	0	0	0	0	0	0	4	0	0	0	0	1
032 B	2	0	33	3	152	4	37	8	3	0	0	0	0	0	0	0	0	0	0	1	1
033 B	5	1	238	11	225	3	74	159	4	0	0	0	0	0	0	4	0	1	0	0	1
038 B	3	1	33	9	155	27	40	59	3	0	0	0	0	0	0	0	0	1	0	0	8
039 B	1	0	14	9	221	21	96	82	2	0	0	0	0	0	0	1	0	0	0	0	3
041 B	1	0	10	3	280	14	102	4	6	0	0	0	0	0	0	0	0	1	0	4	0
042 B	2	0	29	2	246	19	95	51	14	0	0	0	0	0	0	3	0	1	0	0	6
043 B	2	1	30	2	234	8	40	40	9	0	0	0	0	0	0	3	0	1	0	0	3
044 B	1	0	19	6	177	10	50	14	6	0	0	0	0	0	0	2	0	0	0	0	3
045 B	2	0	20	5	89	9	278	10	7	0	0	0	0	0	0	8	0	0	0	1	2
046 B	5	0	41	4	225	4	656	59	8	0	1	0	0	0	7	3	0	0	0	0	1
Blank B	0	0	11	0	20	0	15	0	18	0	0	0	0	0	0	1	0	0	0	0	0
029 C	12	1	43	17	534	15	370	91	14	0	9	0	0	0	1	3	1	1	0	6	6

Sample	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ru	Rh	Pd	Ag	Cd	Sn	Sb	Te	I	Cs
030 C	7	1	116	15	424	8	58	114	13	1	4	0	1	0	1	5	0	0	0	8	1
031 C	10	0	26	13	370	18	36	33	12	1	7	0	0	0	1	3	1	1	0	7	2
032 C	3	0	57	8	349	3	18	9	6	3	7	0	0	0	1	1	5	1	0	16	1
033 C	11	1	724	44	147	4	49	170	69	1	18	0	0	3	2	0	0	1	0	4	4
038 C	7	1	125	52	127	26	41	85	22	0	13	0	0	0	8	0	1	0	1	7	23
039 C	22	1	29	186	130	37	82	177	22	1	6	0	0	0	1	0	1	0	0	1	6
041 C	9	0	31	15	894	22	40	36	19	2	5	0	0	0	1	0	0	1	0	13	1
042 C	9	1	80	30	183	20	28	78	13	1	10	0	0	0	2	0	0	1	0	4	15
043 C	7	1	100	20	184	12	30	45	10	1	8	0	0	0	1	4	0	0	0	3	6
044 C	7	1	57	19	229	16	10	46	3	1	7	0	0	0	1	1	0	0	0	4	5
045 C	18	1	44	5	168	11	530	43	16	2	6	0	0	0	2	0	0	0	0	7	3
046 C	4	0	352	10	139	2	209	16	12	0	8	0	0	0	2	4	1	0	0	5	2
Blank C	1	0	12	0	309	1	17	0	10	0	2	0	0	0	1	1	2	1	0	4	0

Sample	**Ba**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Th**	**U**
029 A	243	97	177	27	89	14	3	14	2	9	1	4	0	3	0	0	0	0	0	0	0	0	0	7	0	89	0	1	2042
030 A	701	16	33	4	16	3	1	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	10	0	62	0	1	0
031 A	862	2	6	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	0	68	0	0	7
032 A	1367	5	13	1	3	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	159	0	2	0
033 A	678	47	114	15	51	9	2	10	1	7	1	3	0	3	0	0	0	0	0	0	0	0	0	4	0	138	0	2	1234
038 A	301	108	263	44	153	28	7	26	3	12	2	5	1	4	1	0	0	0	0	0	0	0	0	3	0	380	0	5	10980
039 A	831	46	61	11	38	6	2	7	1	5	1	3	0	3	1	0	0	0	0	0	0	0	0	2	0	96	0	2	2961
041 A	901	2	3	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	89	0	2	9
042 A	455	7	14	2	6	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	57	0	1	12
043 A	434	20	39	5	17	2	1	2	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	62	0	0	0
044 A	1055	3	7	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	134	0	3	0
045 A	517	5	12	1	4	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	41	0	1	0
046 A	711	111	187	25	82	14	4	17	2	14	3	7	1	6	1	0	0	0	0	0	0	0	0	0	0	121	0	9	8348
Blank A	476	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	97	2	1	2
029 B	341	123	370	42	138	20	5	21	2	14	2	6	1	5	1	0	0	0	0	0	0	0	0	0	0	120	0	1	3952
030 B	998	57	118	14	44	6	2	6	1	4	1	2	0	2	0	0	0	0	0	0	0	0	0	0	0	142	0	1	0
031 B	2400	14	36	2	7	1	1	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	151	0	1	9
032 B	1348	12	33	2	8	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	110	0	1	0
033 B	924	127	302	40	137	22	5	26	3	20	3	10	1	9	1	0	0	0	0	0	0	0	0	0	0	275	0	7	2857
038 B	144	49	127	24	90	16	4	15	2	9	1	4	0	3	0	0	0	0	0	0	0	0	0	0	0	444	0	1	5289
039 B	270	33	39	6	19	2	1	3	0	3	1	2	0	2	0	0	0	0	0	0	0	0	0	0	1	52	0	1	0
041 B	531	4	7	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	98	0	0	6
042 B	719	59	101	13	41	6	2	7	1	5	1	3	0	3	0	0	0	0	0	0	0	0	0	0	0	153	0	1	980
043 B	492	64	129	16	51	7	2	7	1	5	1	2	0	2	0	0	0	0	0	0	0	0	0	0	0	83	0	1	0
044 B	568	18	37	4	12	2	0	2	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	90	0	0	0
045 B	5539	26	57	4	13	2	1	2	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	1	178	0	2	0
046 B	264	60	159	22	78	13	3	12	2	9	2	4	1	4	1	0	0	0	0	0	0	0	0	0	0	167	0	5	3840
Blank B	213	1	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	110	0	0	3
029 C	228	62	220	34	124	24	6	22	2	13	2	6	1	6	1	0	0	1	0	0	0	0	1	0	1	139	0	4	8381

Sample	**Ba**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Th**	**U**
030 C	800	96	243	34	117	19	5	19	2	12	2	6	1	5	1	0	0	1	0	0	0	0	0	0	0	134	0	3	0
031 C	984	44	174	12	41	7	2	6	1	4	1	2	0	2	0	0	0	1	0	0	0	0	0	0	1	127	0	3	0
032 C	301	22	57	4	15	3	1	2	0	1	0	1	0	1	0	0	0	1	0	0	0	1	2	1	0	215	0	1	0
033 C	432	97	280	43	153	30	7	31	4	24	4	11	1	11	1	2	0	2	0	0	0	0	0	0	0	298	1	13	14140
038 C	474	44	123	24	93	20	5	18	2	11	2	5	1	5	1	1	0	3	0	0	0	0	1	0	0	112	2	17	15875
039 C	691	62	94	18	61	11	3	11	1	10	2	6	1	7	1	1	0	1	0	0	0	0	0	0	1	94	0	16	3124
041 C	578	32	69	9	30	5	1	5	1	4	1	2	0	2	0	0	0	1	0	0	0	0	0	0	0	129	0	2	0
042 C	282	89	198	29	97	17	4	15	2	10	2	5	1	5	1	0	0	2	0	0	0	0	23	0	0	60	0	7	5124
043 C	646	56	139	20	65	11	3	10	1	6	1	3	0	3	0	0	0	2	0	0	0	0	2	0	0	109	0	2	3548
044 C	124	47	117	15	49	9	2	8	1	6	1	3	0	3	0	0	0	1	0	0	0	0	1	0	0	121	0	2	431
045 C	1190	94	245	26	80	12	3	10	1	7	1	3	0	3	0	0	0	1	0	0	0	0	1	0	4	117	0	2	0
046 C	291	15	37	6	19	3	1	3	0	2	0	1	0	1	0	0	0	1	0	0	0	0	2	0	0	239	1	4	0
Blank C	330	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	43	0	1	3