TIER 1 RISK ASSESSMENT OF SELECTED RADIONUCLIDES IN SEDIMENTS OF THE MOOI RIVER CATCHMENT

By

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Report To The Water Research Commission on the Project
"Tier 1 Risk Assessment of Radionuclides in Selected Sediments of the Mooi River"

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EXECUTIVE SUMMARY

HISTORICAL BACKGROUND TO THE STUDY

Screening surveys of radioactivity in the Mooi River catchment were conducted by the Institute of Water Quality Studies (IWQS) of the Department of Water Affairs and Forestry (DWAF) in 1995 and 1996 (DWAF 1995, 1996).

Elevated levels of the radionuclides of uranium and radium were detected in streams close to gold mining activities. Many radionuclides of possible concern were not measured, and, in view of the lack of information concerning variability of radionuclide concentrations in the river systems, it was proposed that a full study of the water resources be completed.

In 1997, a monitoring study of radioactivity in the surface- and groundwaters of the Mooi River catchment was conducted, in collaboration with a wide group of interested parties (DWAF, 1999). The study did not consider radioactivity in sediments.

The great majority of sampling sites in the catchment showed low levels of water-borne radionuclides, with a total drinking water dose below 0.1 mSv/year. The sites that showed significant concentrations of water-borne radionuclides were associated with discharge of mine water into the river system. Levels of radioactivity in the water column dropped off with distance from the mining operations, with a greater attenuation of water-borne radioactivity downstream of the mining operations than could be explained by dilution by river water alone.

It was hypothesised that some of the radionuclides were preferentially accumulating in the sediments in the Mooi River system.

MOTIVATION FOR THE STUDY

The sediment phase of aquatic systems is largely unexplored in South Africa. In 1997, the CSIR, in collaboration with IWQS, embarked on a study of the factors influencing metal accumulation in sediments.

From the results of the DWAF and CSIR studies, it was hypothesised that the sediments of the Mooi River (and, therefore, other rivers in South Africa) are accumulating radionuclides from the water column.

The sediment phase is in intimate contact with the water column phase of the aquatic ecosystem. Metals in the aquatic ecosystem are in quasi-equilibrium between sediment and water column phases. This means that the distribution of metals between the sediment and water column phases is governed both by thermodynamics (the relative stability of the metal in each phase), and by kinetics (the rate at which the metals move between phases).

Under typical conditions, the sediment phase binds metals more strongly than the aqueous phase. This means that there is a continuous migration of metal from the aqueous to the sediment phase. Thus, under historical and currently acceptable water management criteria, the water column toxic metal concentrations might be maintained at a safe level for the preservation of health of the water users, while the sediments become enriched with respect to the toxic metals.

Radionuclides may not be highly concentrated in the aqueous column, but they may be absorbed preferentially into the sediment, where they can become available to the water column under scenarios of disturbance.

It is important to know under which conditions the radionuclides may be remobilised, and if this occurs, how much of a risk to human health it may be.

It is envisaged that the current cursory investigation of the radioactivity of the sediments will add to the data required to fully understand the fate of radionuclides in the Mooi River and the risk these radionuclides pose.

DESCRIPTION OF THE STUDY AREA

The region of interest lies South-West of Johannesburg.

The watershed of the Mooi River, encompassing that of the Mooi Rivier Loop and Wonderfontein Spruit, has received the impacts from mining operations for more than sixty years.

The river of interest is the stream called the Mooi Rivier Loop and Wonderfontein Spruit. This stream provides input into the Boskop Dam, from which the town of Potchefstroom derives its drinking water.

The study required a control site, which needed to be near the river of interest, but which was believed to be unimpacted by mining operations. Klerkskraal Dam was chosen, because the dam is fed from a stream emanating from a dolomite eye. There are no mining operations upstream of Klerkskraal Dam, and any contamination the dam experienced would have arrived by an atmospheric route. Contaminants from this potential source were considered to be small in magnitude by comparison to water-borne contaminants arising from the mining operations in the watershed.

Study sites were chosen to be impoundments, where water flow is low, and where there is an opportunity for organic matter to accumulate. Radionuclides of interest may be immobilised under these conditions.

Sites are described in Table E.1.

Table E.1 Sites in study area

Site No.	Site Name	Site Code	Site Description
1	Tudor Dam	(TUD1)	Located at the top of the catchment - dry, and had a crust which resembled a mixture of gypsum and ferric oxide, mixed with organic detritus originating from the reed beds that have cycled through growth and burning for some time.
2	Attenuation Dam	(ATT2)	Lies downstream of Tudor Dam.
3	Donaldson Dam	(DON3)	A recreational dam, where fish are caught for human consumption.
4	Harry's Dam	(HAR5)	Dam directly upstream of Abe Bailey Dam, and Carletonville.
5	Abe Bailey Dam	(ABE4)	Slightly raised above the level of the river of interest, and is only expected to receive input during flood events.
6	The Sluice	(SLU6)	A site where mine water is directly input through a concrete channel into the river.
7	Andre Coetzee's Dam	(A-C7)	Directly downstream of the sluice, and is currently a recreational dam used for fishing and boating. The sediments of this dam are unusually reducing, with copious quantities of methane generation in evidence.
8	Muiskraal	(MUIS10)	On the river, next to a bridge.
9	Boskop Dam	(BOS8)	Downstream of Muiskraal. Main water source for Potchefstroom.
10	Klerkskraal Dam	(KKD9)	Below a dolomitic eye. Upstream of Boskop Dam. Not influenced by Wonderfonteinspruit pollution. Pollution source is not from large mining operations. This site was chosen as the reference site for the catchment.

AIMS OF THE STUDY

The main aim of the present study was to establish if there was a potential threat posed by radionuclides to humans in the Mooi River catchment.

This aim led to the following research questions:

- Have radionuclides (e.g. Uranium) preferentially accumulated in river sediments?
- Can the radionuclides be remobilised under realistic environmental conditions?
- Under what conditions might they be remobilised (i.e. in what form are the radionuclides in the sediments)?

APPROACH IN THE STUDY

The approach adopted in the study involved the following

- Determination of the concentrations of selected radionuclides (^{238}U, ^{235}U, ^{234}U, ^{223}Ra, ^{232}Th, ^{210}Pb and ^{210}Po) in the sediments of the Mooi River (Wonderfonteinspruit and Mooi Rivier Loop) between Krugersdorp and Potchefstroom in the Witwatersrand gold-mining region of South Africa by field gamma spectrometry and by chemical analysis of the sediments.
- Determination of the conditions under which the radionuclides may be remobilised by sequential chemical extraction.
- Determination of the risks represented by potential remobilisation of possible stored radionuclides to man in a Tier 1 risk assessment.

RISK METHODOLOGY EMPLOYED IN THE PRESENT STUDY

Tiers of Risk Assessment for Contaminated Sediments

Sediment Ecological Risk Assessments (SERA's) should be conducted in a tiered or phased approach (Ingersoll *et al*, 1997, USEPA 1992b). An initial analysis (Tier 1) is conducted, using very conservative assumptions about exposure and effects, then a decision is made on how to proceed.

Typically, this initial screening-level risk assessment is conducted using available data and conservative assumptions about effects, or existing effects-based benchmark values or guidelines.

The present study, entitled "Tier 1 Risk Assessment Of Radionuclides In Selected Sediments Of The Mooi River" is explicitly a first-tier risk assessment, in which concentrations of environmental contaminants are compared to benchmarks, such as legislative action levels.

Environmental exposures are viewed as concentrations of parent radionuclides (U-238) measured by direct analysis and by inference from gamma spectroscopy.

Traditional radiological risk calculations involve analysis of scenarios of exposures and uptake, and thus constitute investigations at orders of Tier 2 or higher.

In tiers subsequent to the Tier 1 assessment, additional data may be collected that better define the risk of adverse effects. At each tier, a pass/fail decision is made whether to proceed to advanced tiers, and if so, which methods to employ in the subsequent tiers.

Legislative Framework Guiding the Risk Assessment

National Nuclear Regulator Act

In 1999, the National Nuclear Regulator Act (Act 47 of 1999) was gazetted. Section 36 of this act called for the development of standards for handling nuclear material as follows:

36. (1) The Minister must, on the recommendation of the board, make regulations regarding safety standards and regulatory practices.
(2) Before any regulations are made in terms of subsection (1), the Minister must, by notice in the *Gazett*e, invite the public to comment on the proposed regulations and consider that comment.

Exclusions from the National Nuclear Regulator Act

The exclusion level for radioactive concentration of any single radionuclide in a solid is currently 0.2 Bq/g.

This implies that if a solid material is associated with a human activity, and it has a radiation intensity of below 0.2 Bq/g per radionuclide, the activity is excluded from the Act. Above this exclusion level, it is required that a site-specific hazard assessment is to be performed.

Tier 1 Risk Assessment in the Current Study

The current study uses the Tier 1 Risk Assessment method, with the risk being calculated by the Quotient method, in which the following ratio is calculated:

$$RiskQuotient = \frac{Radioactive\,Concentration\,of\;Radionuclide}{Regulatory\;Exclusion\,Limit\;for\,Radionuclide}$$

$$= \frac{Radioactive\,Concentration\,of\;Radionuclide}{0.2Bq/g}$$

RISK ASSESSMENT

Scenarios Modelled

The following chemical scenarios were considered.

- Resuspension of sediment into water of existing quality (as measured on the sampling trip). This is also equivalent to infiltration of overlying water of current quality into sediment by hydraulic head.
- Infiltration of surface water into sediment of quality represented by extremes of pH historically observed.
- Movement of the redox profile due to bioturbation or input/decrease of carbon.
- Significant elevation of redox potential by exposure to atmospheric oxygen.

These scenarios were all superimposed on the following calculated Eh-pH diagrams.

Scenario Evaluation

Scenarios Simulated by Chemical Equilibrium Modelling

In all scenarios considered, there was the possibility of uranium being solubilised by environmental processes that fall within the bounds of reason. The scenario under which uranium is least likely to be mobilised is that of strongly reducing environmental conditions.

The scenario under which uranium is most likely to be solubilised is that of high oxidation potential and low- to intermediate pH. This scenario is likely if the sediments of an impoundment are exposed by drainage, or by dredging operations. Increased oxidation potential automatically enhances the potential for low pH conditions.

Thorium is expected to remain in the chemically inert fraction, and transport of thorium is most likely to be as a particulate with comparatively limited migration potential.

Scenarios Simulated by Sequential Chemical Extraction

In all of the sediments tested, uranium was mobilised by reaction with weak acid. Uranium was also mobilised by increase in oxidation potential, and by decrease in oxidation potential.

Thorium was not expected to be extracted significantly in the extraction procedures. There is evidence that thorium remained in the inert fraction of the sediments.

Scenarios Observed in Field Site Assessments

There is evidence that uranium is transported in a soluble form along the length of the Wonderfontein Spruit and Mooi Rivier Loop. Uranium is input at defined sources, e.g. Tudor Dam and the Sluice, and it reports at localities downstream where one would not expect particulates to reach (i.e. they may be filtered by reed beds).

There is evidence that uranium is transported from the Sluice into Andre Coetzee's dam, where it is currently largely immobilised by the low oxidation potential in the dam.

CONCLUSIONS

The main aim of the study was to determine possible risks to humans of radionuclides in the sediments of the Mooi River catchment.

The study answered the research questions as follows:

- Radionuclides have been found to accumulate in the sediments of the Mooi River catchment.
- The main radionuclide of interest, being uranium, seems to be adsorbed to the environmental phases: carbonate, iron and manganese oxyhydroxides, and organics (with a slight possibility of being included in sulphide components).
- Uranium may be remobilised into the water column by perturbation of TDS, pH or oxidation potential.

The criterion for the Tier 1 Risk Assessment was the 200 Bq/kg limit stipulated by the Nuclear Energy Act of 1993 for unconditional deregulation of sites.

The sites Tudor Dam (TUD1), Attenuation Dam (ATT2), Donaldson Dam (DON3), Harry's Dam (HAR5), Sluice (SLU6) and Andre Coetzee's Dam (A-C7) had U-238 levels higher than the Nuclear Energy Act (1993) stipulation, and, therefore, had a positive Tier 1 Risk Quotient.

The sites are ranked in order of increasing Tier 1 risk as follows:

Highest Tier 1 Risk Quotient	Tudor Dam
	Andre Coetzee's Dam
	Sluice
	Attenuation Dam
	Donaldson Dam
Lowest Tier 1 Risk Quotient	Harry's Dam

RECOMMENDATIONS

The objective of a Tier 1 Risk Assessment is to determine whether or not more detailed investigations are required.

Thus, it is recommended that a more detailed exposure assessment be conducted for the following impoundments, in the order of risk from highest to lowest, as indicated above. A Tier II risk assessment would involve determining sources of radionuclides and pathways of radionuclides to man.

The chemical and hydro-dynamics of the catchment should be monitored over a year, in order to better model contaminant transport in the catchment.

A theoretical model of Potchefstroom's water treatment works should be constructed, to assess the ability of Potchefstroom to treat possible radionuclides flushing into the water source.

Considering the proximity of Andre Coetzee's Dam to the Boskop Dam, it is recommended that the extent of uranium deposition in Andre Coetzee's dam be assayed.

Uranium is immobilised in this dam by environmental processes that buffer the pH at a high level and the redox at a low level. The extent of this buffering capacity should be known in order to evaluate the risks of re-release of U-238 during possible dredging operations.

ACKNOWLEDGEMENTS

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

"TIER 1 RISK ASSESSMENT OF RADIONUCLIDES IN SELECTED SEDIMENTS OF THE MOOI RIVER"

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

Mr P Herbst	Water Quality Management, Department of Water Affairs & Forestry
Dr PL Kempster	Institute for Water Quality Studies, Department of Water Affairs & Forestry
Ms MC Eksteen	Water Quality Management, Department of Water Affairs and Forestry
Dr AH Leuschner	Gold Fields Limited
Prof FB Waanders	School of Chemical and Minerals Engineering, PU for CHE
Dr D Wymer	Chamber of Mines
Mr A McLaren	Lower Wonderfonteinspruit Forum
Mr H Coetzee	Council for Geosciences
Dr F Winde	University of Jena, East Germany
Dr S Woodborne	Environmentek/CSIR

The financing of the project by the Water Research Commission and the CSIR Parliamentary Grant, and the contribution of the members of the Steering Committee is acknowledged gratefully.

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INTRODUCTION

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The study did not consider radioactivity in sediments.

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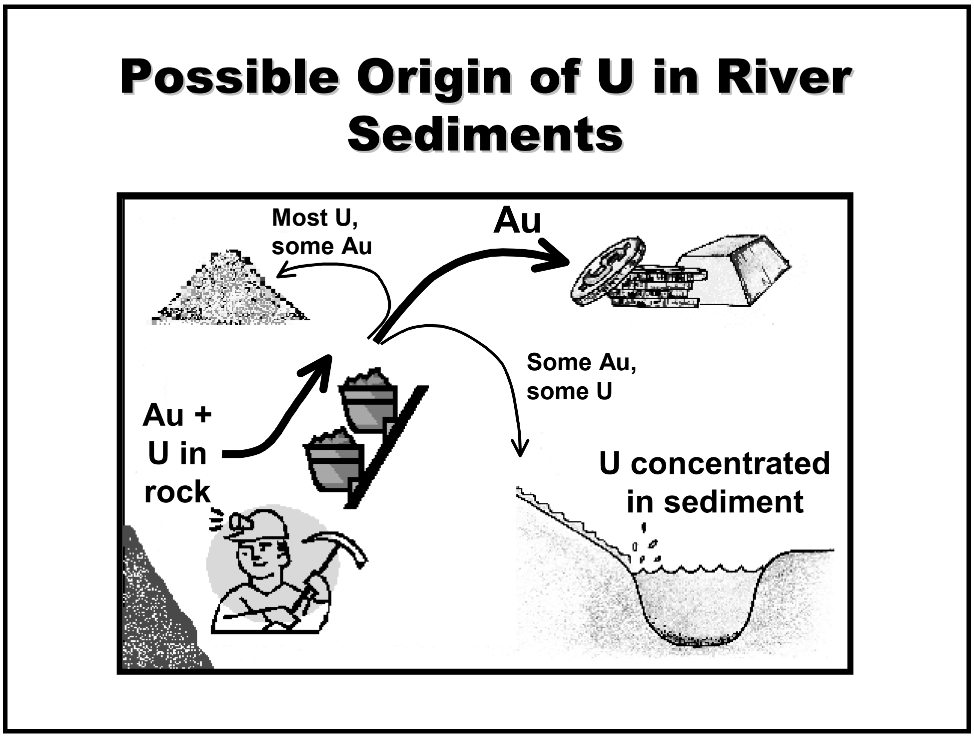
A preliminary mass balance on the data from the DWAF (1999) study suggested that there was a greater attenuation of water-borne radioactivity downstream of the mining operations than could be explained by dilution by river water alone.

It was hypothesised that some of the radionuclides were preferentially accumulating in the sediments in the Mooi River system.

Figure 1 graphically illustrates the possible origin of uranium in the river system



Possible Origin of U in River Sediments

Figure 1 Graphical representation of the fate of metals derived from gold mining operations.

MOTIVATION FOR THE STUDY

The sediment phase of aquatic systems is largely unexplored in South Africa.

In 1997, the CSIR, in collaboration with IWQS, embarked on a study of the factors influencing metal accumulation in sediments. A summary of the information compiled in this study (Wade *et al.*, 1999) is presented in Appendix 1.

From the results of the DWAF and CSIR studies (see above), it was hypothesised that the sediments of the Mooi River (and, therefore, other rivers in South Africa) are accumulating radionuclides from the water column.

The Technical Committee for Radioactivity Monitoring Programme has focused attention on the soluble water column constituents of the Mooi River, and has amassed a large database of water-column radiological data (DWAF, 1999). Of the 41 sites monitored, 39 showed an ideal or acceptable water quality for a lifetime of drinking water, based on measurement of the soluble water column constituents. Only two sites showed significant elevation of radiation dose over background in the water column. Explicit in the study was the focus on the soluble fraction of the water column, and it was explicitly mentioned that the sediments had been neglected from the study.

The sediment phase is in intimate contact with the water column phase of the aquatic system. Metals in the aquatic system are in quasi-equilibrium between sediment and water column phases. This means that the distribution of metals between the sediment and water column phases is governed both by thermodynamics (the relative stability of the metal in each phase), and by kinetics (the rate at which the metals move between phases).

Under typical conditions, the sediment phase binds metals more strongly than the aqueous phase. This means that there is a continuous migration of metal from the aqueous to the sediment phase. Thus, under historical and currently acceptable water management criteria, the water column toxic metal concentrations might be maintained at a safe level for the preservation of health of the water users, while the sediments become enriched with respect to the toxic metals.

Radionuclides may not be highly concentrated in the aqueous column, but they may be absorbed preferentially into the sediment, where they can become available to the water column under scenarios of disturbance.

In one scenario, the general chemical conditions of the aquatic system can remain constant. This means that water column concentrations of the radioactive metals are maintained at a safe level, but metal enrichment by the sediment results in high uptake of radionuclides by sediment dwellers. Sediment dwellers can be exposed to the metals by two major exposure routes: migration of metals from the occluded sediment water (pore water) into the biota; and exposure through ingestion of the sediment. Which exposure route dominates depends very much on the feeding and respiration habits of the individual organisms.

In another scenario, the aquatic system might be disturbed. There might be drastic changes in pH, redox status, or there can be an event as mundane as a flood event disturbing the sediments such that they might become suspended in the water column, which has chemical conditions sometimes vastly differing from those of the bottom sediment. Under this scenario, metals that were once immobilized in the sediment might become mobilized into the water column, resulting in a pulse of metals in the water column.

It is important to know under which conditions the radionuclides may be remobilised, and if this occurs, how much of a risk to human health it may be.

This latter scenario applies also to the practise of dredging of sediments. The movement of sediment from one environment to another will change the chemical environment of the sediment, and therefore the sediment's chemical characteristics, with concomitant implications on the mobilization of accumulated metals.

While previous methods for managing aquatic systems involved consideration of fixed chemical concentration limits (deterministic method), there is a move towards Risk-based management (probabilistic) strategies. One such tool under consideration by the Department of Water Affairs and Forestry is Ecological Risk Management.

In order to manage risk one needs to have a means of predicting the fate and effects of chemicals in the environment according to some model. In order to develop and use such a model one needs to have a proper understanding of the dominant processes controlling the distribution of a chemical in the environment.

It is envisaged that the current cursory investigation of the radioactivity of the sediments will add to the data required to fully understand the fate of radionuclides in the Mooi River and the risk these radionuclides pose.

AIMS OF THE STUDY

The main aim of the present study was to establish if there was a potential threat posed by radionuclides to humans in the Mooi River catchment.

This aim led to the following research questions, which are graphically posed in Figure 2.

- Have radionuclides (e.g. uranium) preferentially accumulated in river sediments?
- Can the radionuclides be remobilised?
- Under what conditions might they be remobilised (i.e. in what form are the radionuclides in the sediments)?

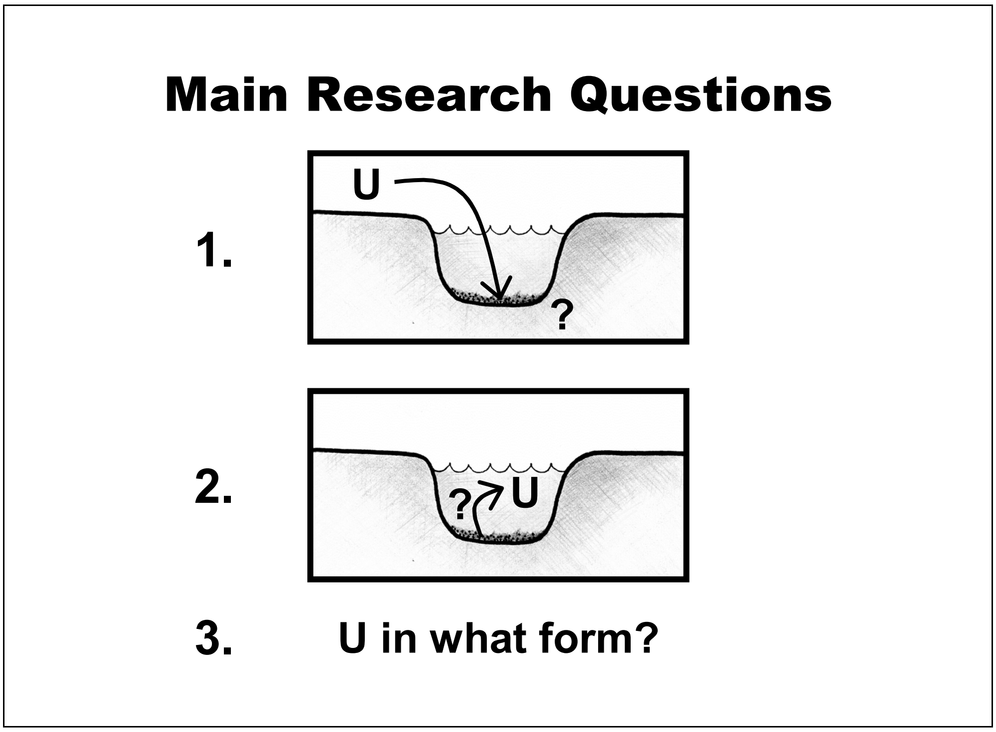


Figure 2 Graphical Summary of Main Research Questions in the Current Study.

APPROACH IN THE STUDY

The approach adopted in the study involved the following

- Selection of sites on the rivers based on the belief that the highest accumulation of radionuclides would occur in relatively stagnant, anoxic zones.
- Determination of the concentrations of selected radionuclides (^{238}U, ^{235}U, ^{234}U, ^{223}Ra, ^{232}Th, ^{210}Pb and ^{210}Po) in the sediments of the Mooi River (Wonderfonteinspruit and Mooi Rivier Loop) between Krugersdorp and Potchefstroom in the Witwatersrand gold-mining region of South Africa by field gamma spectrometry and by chemical analysis of the sediments.
- Determination of the conditions under which the radionuclides may be remobilised by sequential chemical extraction.
- Determination of the potential remobilisation of possible stored radionuclides to man in a Tier 1 risk assessment.

Traditional determination of the risks to human health involves investigation of exposure pathways, which is not an appropriate activity in a Tier 1 risk assessment.

The Tier 1 risk assessment involves measurement of some parameter which may contribute to exposure, and comparison to a benchmark, frequently a regulatory guideline. This procedure was adopted here, - a comparison between an environmental activity of a radionuclide, and a regulatory guideline, as is explained in the following section.

METHODOLOGY OF TIER 1 RISK ASSESSMENTS

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Tiers of Risk Assessment for Contaminated Sediments

Sediment Ecological Risk Assessments (SERA's) should be conducted in a tiered or phased approach (Ingersoll *et al*, 1997, USEPA 1992b). An initial analysis (Tier 1) is conducted, using very conservative assumptions about exposure and effects, then a decision is made on how to proceed.

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Environmental exposures are viewed as concentrations of parent radionuclides (U-238) measured by direct analysis and by inference from gamma spectroscopy.

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In tiers subsequent to the Tier 1 assessment, additional data may be collected that better define the risk of adverse effects. At each tier, a pass/fail decision is made whether to proceed to advanced tiers, and if so, which methods to employ in the subsequent tiers.

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Tier 1 Risk Assessment in the Current Study

The current study uses the Tier 1 Risk Assessment method, with the risk being calculated by the Quotient method, in which the following ratio is calculated:

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STRUCTURE OF THE REPORT

The “Materials and Methods” section examines practical considerations of sediment sampling and analysis, and details the protocols used in the current study.

Scenarios for immobilization and re-release are probed by chemical modelling simulations in the subsequent section on radionuclide environmental fate modelling.

The practical aspects of the study are introduced in a description of the study area, followed by analysis of the radiological data in terms of ratios of activities and radionuclide concentrations derived by various methods.

The total concentration of U-238 is evaluated at each site sampled.

In conclusion, a Tier 1 risk estimate is obtained for the sites sampled, and some recommendations are tabled.

The discussion of general aspects of risk assessment is presented in an appendix. The discussion is general, and narrows down to the type of risk assessment used in the current study.

The current knowledge of chemical characteristics of sediment components are discussed in an appendix, with a view to understanding the general metal-binding qualities of sediments.

DESCRIPTION OF THE STUDY AREA

The region of interest lies South-West of Johannesburg. The region is depicted on the map in Figure 3.

The watershed of the Mooi River, encompassing that of the Mooi Rivier Loop and Wonderfontein Spruit, has received the impacts from mining operations for more than a hundred years.

The river of interest is the stream called the Mooi Rivier Loop and Wonderfontein Spruit. This stream provides input into the Boskop Dam (site *BOS8*), from which the town of Potchefstroom derives its drinking water.

The study required a control site, which needed to be near the river of interest, but which was believed to be unimpacted by large mining operations. Klerkskraal Dam (*KKD9*) was chosen, because the dam is fed from a stream emanating from a dolomite eye. There are no large mining operations upstream of Klerkskraal Dam, and any contamination the dam experienced would have arrived by an atmospheric route. Contaminants from this potential source were considered to be small in magnitude by comparison to water-borne contaminants arising from the mining operations in the watershed upstream of the Boskop Dam.

Study sites were chosen to be impoundments, where water flow is low, and where there is an opportunity for organic matter to accumulate. These are the conditions under which radionuclides of interest may be retained (See "Methodology for Site Selection" in "Materials and Methods").

Site numbers are presented in Table 1. The GPS coordinates of all the sites are given in Appendix 7.

Table 1 Sites in study area

Site No.	Site Name	Site Code	Site Description
1	Tudor Dam	(TUD1)	Located at the top of the catchment - dry, and had a crust which resembled a mixture of gypsum and ferric oxide, mixed with organic detritus originating from the reed beds that have cycled through growth and burning for some time.
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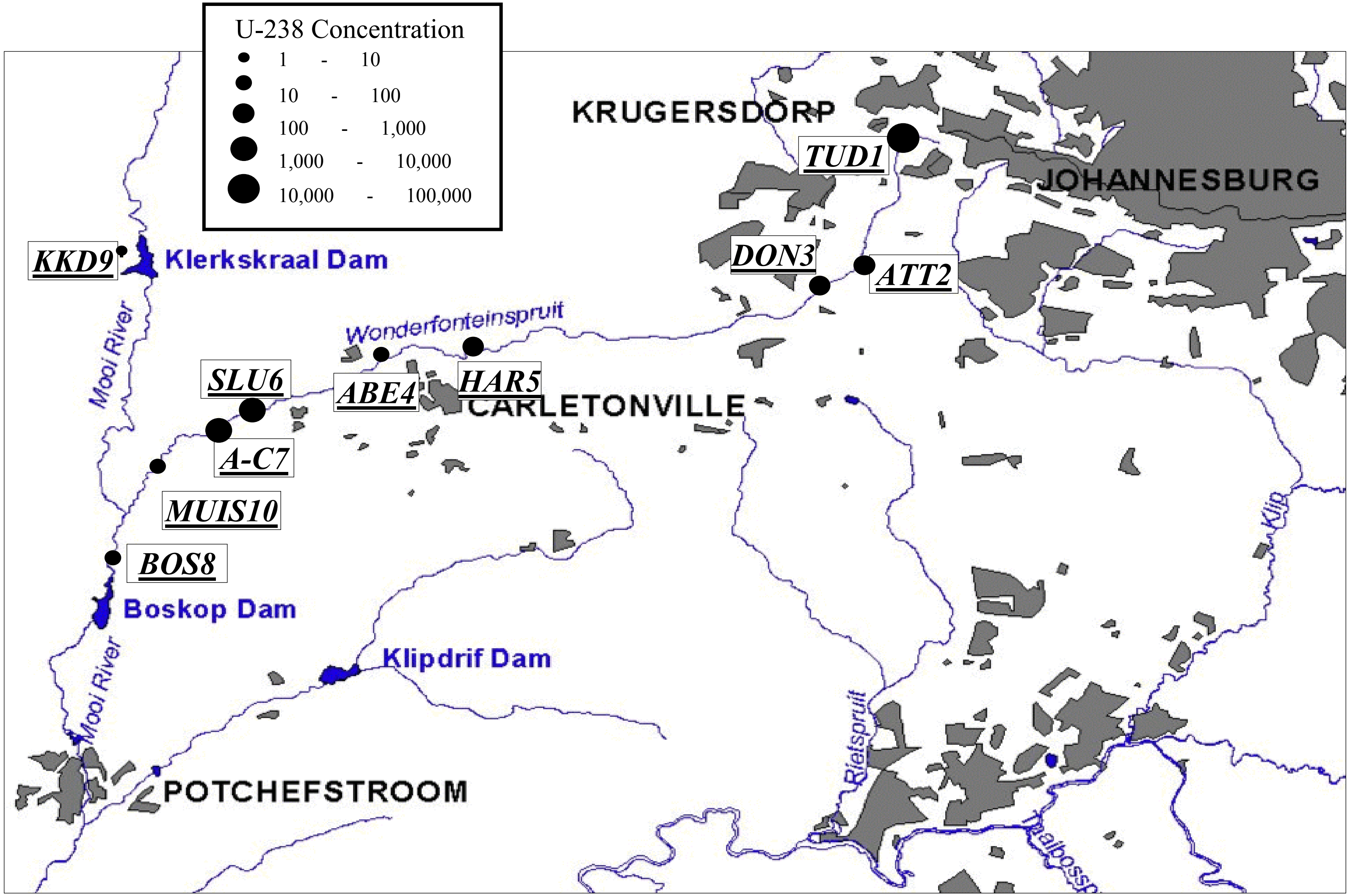


Figure 3: Study area. Sites sampled are labelled in italics and underlined. Site markers are scaled to represent the concentration of ^{238}U in the sediments.

MATERIALS AND METHODS

METHOD OF SITE SELECTION

Sites were sampled during winter, the dry season, for reasons of hydrology – the river flows were low, permitting safe sampling, and easy access to sediments in impoundments. In addition, temperatures are lower, enhancing oxygen content of the rivers, and possibly leading to less stability of metals in sediments.

The sites that were sampled along the river were chosen on the basis of known chemistry of sediments with respect to metal binding (see Appendix 1).

Since the objective of the study was to determine if there was a Tier 1 risk posed by radionuclides in the sediments of the Mooi River catchment, sites were determined on the basis of expected high concentrations of radionuclides.

Requirements for immobilization and retention (accumulation) of radionuclides are as follows:

- Chemically reducing environment.
- Suspected accumulation of fine organic matter and inorganic particles.
- Deposition of particles by low flow hydraulic regimes.

The conditions described above naturally led to the investigation of impoundments where the hydraulic conditions were such that water flow was slowed dramatically, and where organic detritus and small inorganic particles could accumulate.

These were also the optimum conditions for field gamma spectrometry.

PROCEDURE FOR SEDIMENT SAMPLING, HANDLING AND STORAGE

General considerations in sediment sampling are summarised in Appendix 2.

Procedures for sediment sampling, handing and storage are graphically represented in Figure 4.

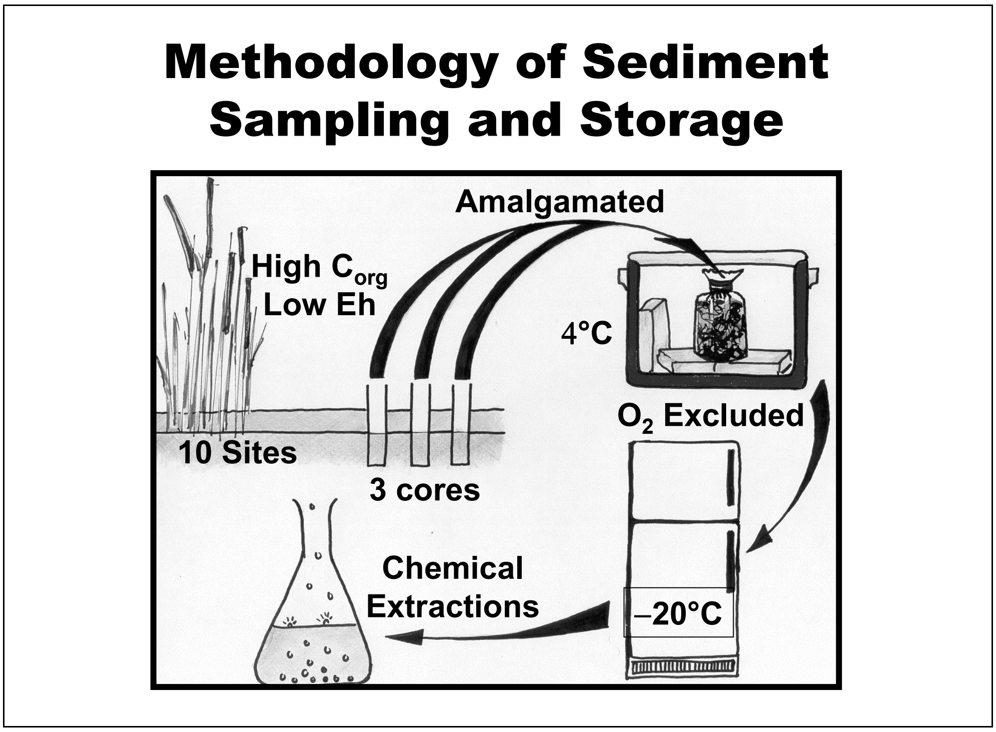


Figure 4 **Graphical summary of sediment sampling and storage**

The river sediments were sampled by slowly inserting a perspex tube of 60mm diameter into the sediment. A valve attached to the top of the perspex tube created a suction when the tube was withdrawn, and a “core” of sediment was thus extracted.

When the perspex core cleared the river bed by a few centimetres, a rubber bung was inserted into the bottom of the perspex tube to contain the sediment. If the sediment contains an appreciable fraction of sand, the sediment leaks out if the bung is not inserted immediately.

The sediment core was extruded using a plunger, until 5 centimetres of sediment remained in the perspex coring tube, whereupon a thin polyethylene plastic bag (such as those used for keeping sandwiches) was wrapped around the perspex tube. The remainder of the core was quickly extruded into the plastic bag, which was then manually squeezed to exclude all bubbles of air.

A composite sample was obtained from three samples at each site, all of which were extruded from the corer into the same plastic bag.

The thin plastic bag was sealed by tying the top with string. A label was placed on the bottom left edge of the plastic bag.

The thin plastic bag was then placed in a thick, durable , ziplock bag. As much air as possible was excluded before sealing the ziplock, because incorporated air might slow down refridgeration. The ziplock bag had a label placed on the bottom left corner.

The labelled ziplock bag, with sample bag inside, was immediately transferred to a cooler box with ice-bricks in it, for temporary storage in the field. The objective was to retard the oxidation of the sulphide or organic components, by the unavoidable bubbles of air that enter the sediment during sampling.

The samples were transported as quickly as possible to a deep freezer, where the samples were frozen for storage, prior to being analysed.

The labels on the plastic sample bags were constructed as follows:

Necessary site information was written onto masking tape with a black felt-tipped pen. The label was cut from the roll and applied gently while the bags were empty. The information on the label included the date, the time, the project code and the site code. All this information was duplicated on a field data sheet.

PROCEDURE FOR SEQUENTIAL CHEMICAL EXTRACTION OF SEDIMENTS

The sequential extraction scheme of Ure et al. (1993) was followed. All extractions were carried out in 250 mℓ glass centrifuge tubes. Stirring with a glass rod and ultra-sound treatment ensured proper mixing of sediment and extraction solution. Suspensions were centrifuged at 3 000 r/min for 30 min subsequent to each extraction step and the extracted metals then separated from the residual sediment by decantation. The solutions of fractions 1 and 2 were filtered through plugs of glass wool to remove biological material.

The extraction procedure used is summarised graphically in Figure 5.

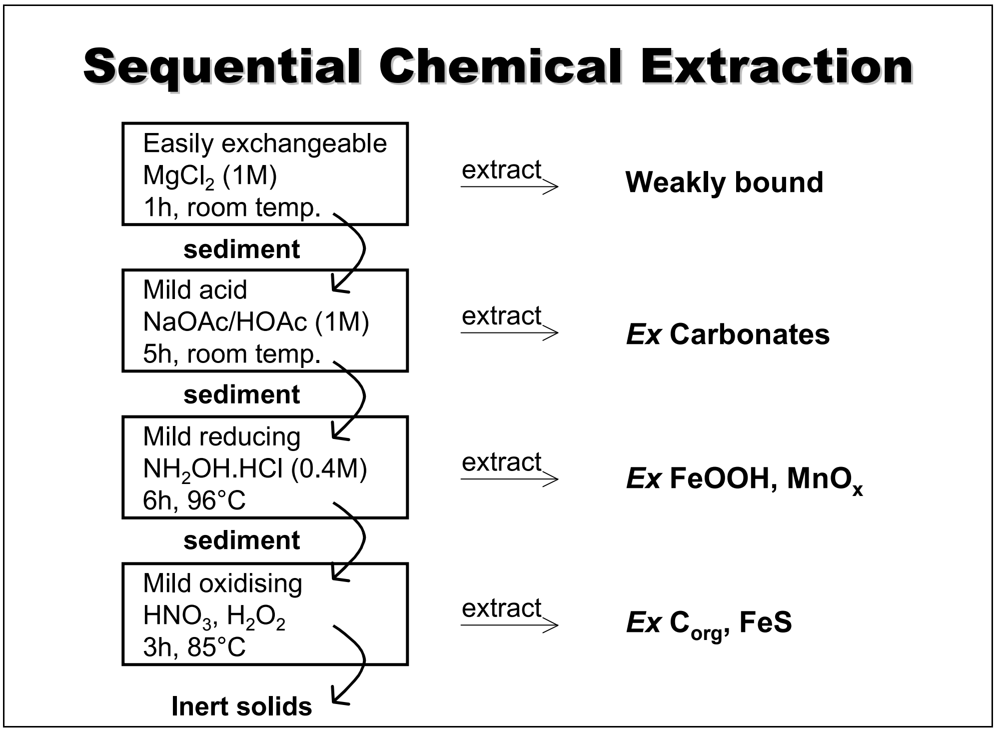


Figure 5 Graphical representation of sediment sequential extraction used in the current study, with phase from which metals are extracted depicted on the right of the diagram

Fraction 1: Exchangeable

~10 g of sediment was extracted at room temperature for 1 h with 80 mℓ magnesium chloride solution (1 M $MgCl_2$, pH 7).

Fraction 2: Bound to carbonates

The residue from Fraction I was leached with 80 mℓ 1 M sodium acetate/acetic acid buffer at pH 5 for 5 h at room temperature.

Fraction 3: Bound to iron and manganese oxides

The residue from Fraction 2 was extracted under mild reducing conditions with 200 mℓ of 0.4 M hydroxylamine hydrochloride ($NH_2OH.HCI$) in 25% (v/v) acetic acid at 96 ±3°C in a water bath for 6 h.

Fraction 4: Bound to organic matter

The residue from Fraction 3 was treated with 30mℓ 0.02 M nitric acid and 50 mℓ 30% (v/v) hydrogen peroxide. The mixture was heated to 85 ± 2°C in a water bath for 3 h. After cooling, 50 ml of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added to the sample and diluted to 200 ml.

The above extracted liquors were submitted to the Atomic Energy Corporation for radiological analysis.

The inert residual fraction was not submitted for radiological assay, the rationale being that the study was concerned with the potentially chemically remobilised radionuclides, as opposed to the inert phase, which would simply be transported by hydrological forces.

PROCEDURE FOR RADIOMETRIC ANALYSIS

The following procedure was taken from the analytical report presented in Appendix 8.

Initial sample preparation

Filtration of the samples was not necessary. The leachate samples were diluted with distilled water to a total volume of 2 litres. This was necessary since each analytical method requires between 100 and 500 mℓ of sample. The dilution factor of approximately 20 implies that, unfortunately, the determination limits also increased by the same factor.

Residual liquid fraction

Preparation: -The residual liquid fraction is subdivided for the different analyses.
Analyses: -Preconcentration of radium, followed by α-particle spectrometry (24h counting time) in a low-background counting facility.
-Uranium and thorium analyses by ICP-MS.
-Preconcentration of Pb/Po-210, followed by α-particle spectrometry (24h counting time) in a low-background counting facility.
Data read: -Determination of the ^{226}Ra, ^{224}Ra and ^{223}Ra-activities.
-Determination of the ^{238}U- , ^{235}U-, ^{234}U- and ^{232}Th-activities.
-Determination of the ^{210}Pb- and ^{210}Po-activities.

Presentation of Analytical Results

The analytical results are presented as Appendix 8. Raw data with the minimum detectable activity (MDA-) values are provided.

The reported uncertainty is a probable error calculated mainly from the counting statistics, and is not the normal standard deviation on replicate analyses.

METHODOLOGY FOR FIELD GAMMA SPECTROMETRY

In-situ gamma radiation spectral measurements were made in the immediate vicinity of the sediment samples. Another "background" measurement was taken from a nearby location that was assumed to be far enough from the river to be minimally contaminated, but close enough to reflect the local geology. In this way a proxy measurement of the degree of gamma radiation was obtained.

The gamma spectra were measured in the range 0-3kEV. In this range, the peaks from ^{214}Bi and ^{208}Tl correspond to the daughter products of the U and Th decay chains. In addition, the ^{40}K peak is a direct measure of the K. These peaks fall into the upper range of gamma energies that are derived from environmental isotopes and it is a relatively simple exercise to "strip" the Compton continuum contributions of any higher energy emitters from these peaks.

The gamma peaks that are used in the stripping exercise are from the daughter products of U and Th, and not directly from the U and Th. The elemental concentrations that are calculated from the stripping assume that all the daughter products are in equilibrium with the parent elements.

In a closed system it takes many thousands of years for secular equilibrium to be reached from pure U. This is unlikely to be the case in the Mooi River and an excess of parent U and Th is expected. The gamma measurements therefore yield minimum values for the parent concentration.

The stripping factors for the spectrometer used in this analysis were calibrated at the Lanseria Airport facility near Pretoria. These are concrete slabs of known radiation that are designed to simulate an infinite matrix.

Calibration is therefore accomplished using 2π (hemispherical) geometry, in which the detector is placed on top of the calibration slab and measures the radiation from a hemisphere of approximately 30 cm radius immediately below the detector.

The field measurements were taken by inserting the detector into the sedimentary matrix. Under these conditions, depending on the depth of insertion of the probe into the sediment, the measurements reflect the radiation from a volume between a hemisphere and a sphere of 30 cm radius (4π geometry) from the detector.

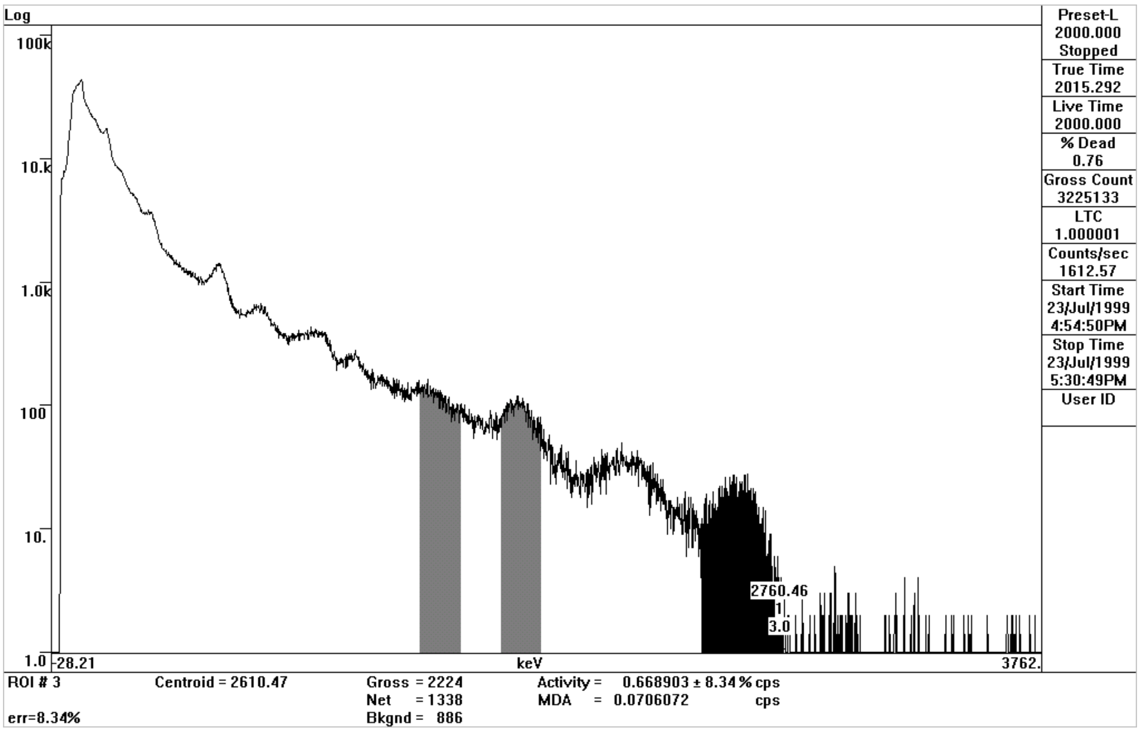
If the radioactive elements in the sediment are uniformly distributed through the matrix, and the probe were deep enough, then the derived concentrations of K, U and Th based on the incident radiation will be over-represented by a factor of 2, if no correction is made for the fact that radiation input is from a sphere, not a hemisphere.

However, it is unlikely that the sample sites meet the uniform distribution criteria, particularly in areas where sediments were laminated or where rocks, boulders and bedrock were in the immediate vicinity of the probe during measurements. The radioisotopes in the sediment are likely to be in high concentration pockets interspersed through the matrix.

The radioactivity in the high concentration pockets reflects the local chemistry and the potential to concentrate pollutants. In the strictest sense, the derived full chain equilibrium concentrations reflect the entire matrix and may be double the true concentrations, but the halved values should be considered to be minimum concentrations.

The gamma-derived U, Th and K values for the Mooi River sediments are presented in Appendix 9. The K is normally derived from clays and feldspars in the sediment. Within the errors that might be expected from the stripping exercise all the K values are within the range of typical surface sediments.

A typical gamma spectrum is presented below as Figure 6.



Preset-L
2000.000
Stopped
True Time
2015.292
Live Time
2000.000
% Dead
0.76
Gross Count
3225133
LTC
1.000001
Counts/sec
1612.57
Start Time
23/Jul/1999
4:54:50PM
Stop Time
23/Jul/1999
5:30:49PM
User ID

ROI # 3
Centroid = 2610.47
Gross = 2224
Net = 1338
Bkgnd = 886
Activity = 0.668903 ± 8.34 % cps
MDA = 0.0706072 cps
err=8.34%

Figure 6 Gamma spectrum from Tudor Dam. Ranges of gamma energies corresponds to emissions from radionuclides as follows: 1380-1530 keV = ^{40}K = 1460.75 keV; 1690-1840 keV = ^{214}Bi (in U chain) = 1764.51 keV; 2460-2760 keV = ^{208}Tl (in Th chain) = 2614.47 keV

PROCEDURES FOR ENVIRONMENTAL FATE MODELLING OF RADIONUCLIDES

The chemical equilibrium-modelling package used was the Joint Expert Speciation System (JESS) (May and Murray, 1991a,b; 1993), which is a sophisticated suite of programs for speciation modelling, developed as a collaborative venture between the CSIR (formerly the Council for Scientific and Industrial Research) in South Africa, and Murdoch University in Western Australia.

JESS allows chemical equilibrium models to be developed for very complex aqueous systems, and has been used in a number of environmental applications, including the modelling of fate of toxic metals (e.g. Mn^{2+}, Hg^{2+}) in industrial effluent systems and prediction of radionuclide solubility in groundwater and seawater.

The thermodynamic database used in the fate simulations was the CHEMVAL (Read, 1990,1991) database, consisting of 332 reactions involving solids, and 565 reactions involving aqueous species of importance to radionuclide fate predictions. CHEMVAL is the European project aimed at unifying thermodynamic databases of reactions concerning radionuclides, and the database has been used in numerous post-closure radiological risk assessments in the UK.

RISK METHODOLOGY EMPLOYED IN THE PRESENT STUDY

The present study, entitled “Tier 1 Risk Assessment Of Radionuclides In Selected Sediments Of The Mooi River” is explicitly a first-tier risk assessment, in which environmental concentrations are compared to benchmarks, such as legislative action limits.

Environmental exposures are viewed as concentrations of parent radionuclides (U-238) measured by direct analysis and by inference from gamma spectroscopy.

The “effects” used in this risk assessment are thus the NNR’s regulatory exclusion limit of 0.2 Bq/g.

The risk assessment method used in this first tier is the Quotient method, in which the quotient is calculated:

$$RiskQuotient = \frac{Radioactive\,Concentration\,of\ Radionuclide}{Regulatory\ Exclusion\,Limit\ for\,Radionuclide}$$

$$= \frac{Radioactive\,Concentration\,of\ Radionuclide}{0.2\ Bq/g}$$

The methodology of the Tiered approach to risk assessments is presented in the Introduction.

General considerations with respect to risk estimation are presented in Appendix 3.

RESULTS OF THE INVESTIGATION

SEQUENTIAL CHEMICAL EXTRACTIONS

Masses used in sequential chemical extractions are presented in Appendix 4.

The results of the sequential chemical extractions may be summarised in Figure 7:

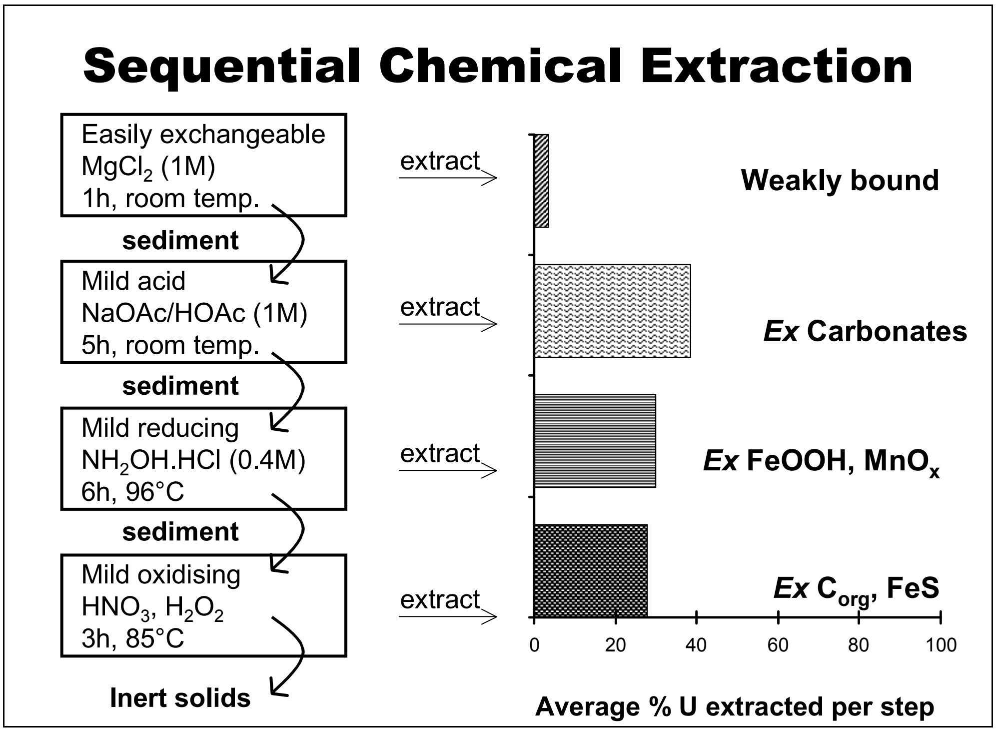


Figure 7 Graphical representation of the average %U extracted per step in the sediment sequential extractions

RESULTS OF RADIOANALYSIS ON SEQUENTIAL CHEMICAL EXTRACTS

The raw analytical data as received from the Atomic Energy Corporation are presented in Appendix 8.

FIELD GAMMA SPECTROMETRY

Results of the field gamma measurements are presented in Appendix 9.

RADIONUCLIDE ENVIRONMENTAL FATE MODELLING

REACTIONS CONSIDERED IN ENVIRONMENTAL FATE MODELLING

The types of chemical reaction considered in the current study are summarised in Figure 8.

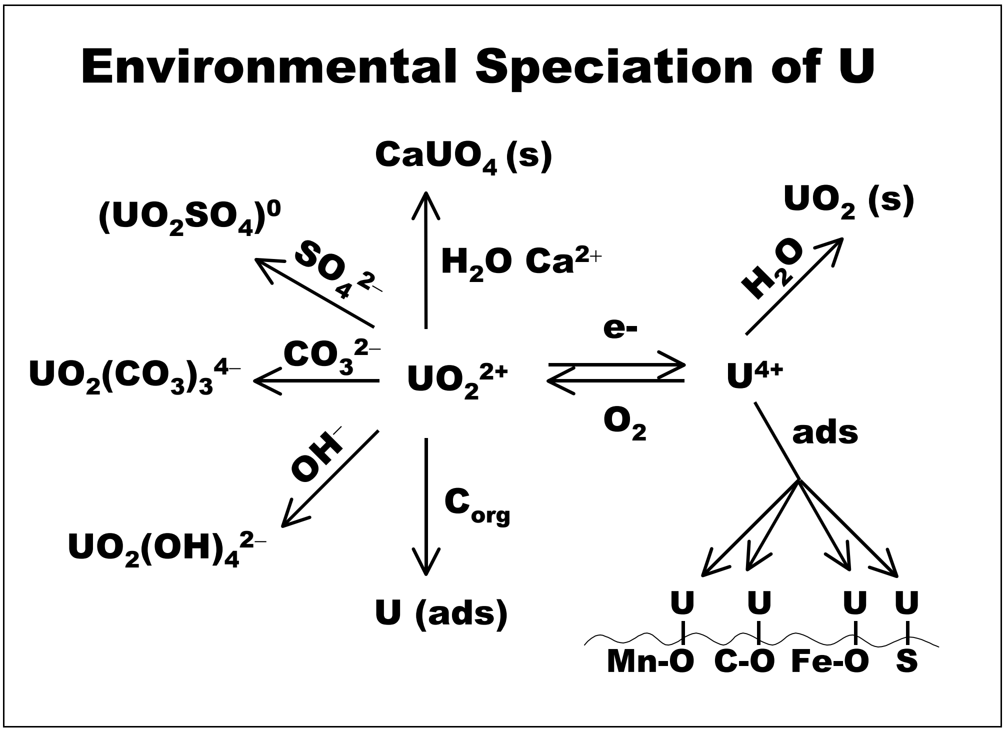


Figure 8 Summary of types of chemical reaction modelled, using uranium chemistry as an example

MODEL FOR AVERAGE RIVER WATER IN THE CATCHMENT

The CSIR database in the program “Water Quality on Disk” was used to obtain estimates of water quality for input into the fate models. This database encompasses all of the measurements of river water quality made by the Department of Water Affairs and Forestry.

Sites were identified on the Mooi Rivier Loop, and the Wonderfontein Spruit. The summary statistics for the sites were downloaded. Mean water chemistry statistics were used for input to the fate model. These means were computed over both time and space for the catchment.

The maximum and minimum values for the water chemistry variables were used in scenario assessments. The data are tabulated in Appendix 6.

THEORETICAL DEPTH PROFILE OF OXIDATION POTENTIAL

The oxidation-reduction potential (redox potential) of a chemical system depends on the dominant chemical reactions that involve electrons. Park and Jaffe (1996) developed a model for predicting the depth profile of redox potential in sediments, based on various scenarios. The theoretical depth profile of redox potential is shown in Figure 9.

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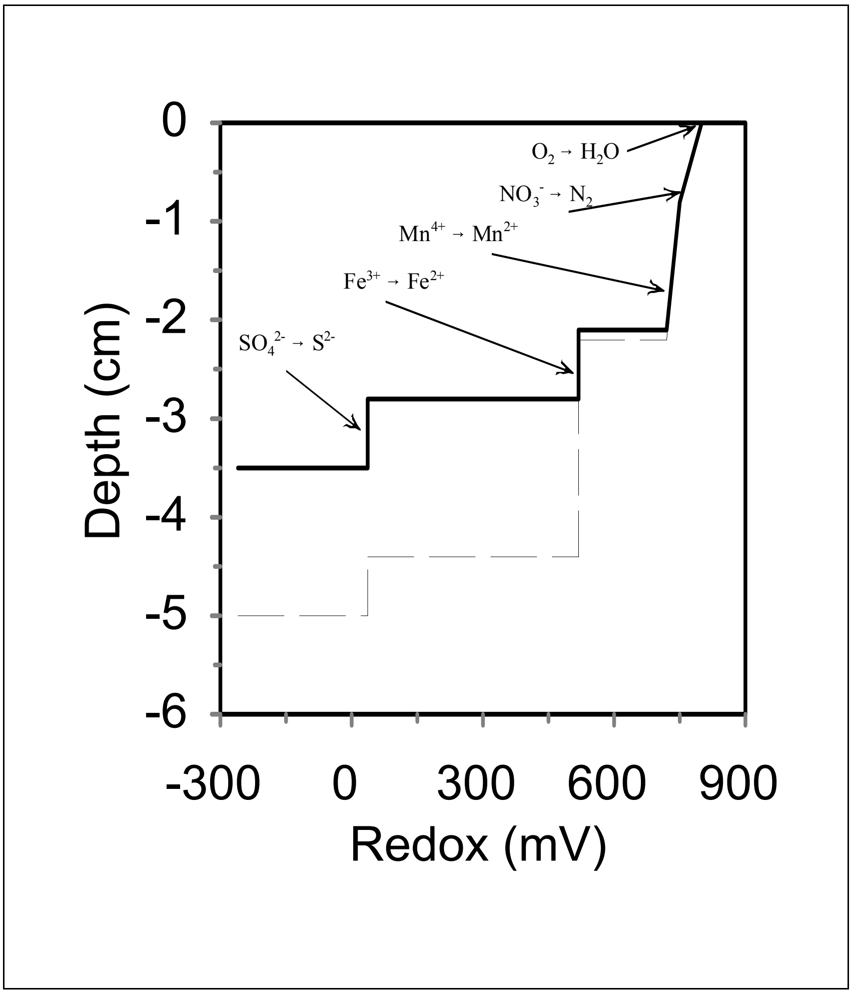


Figure 9 Theoretical redox depth profiles from Park and Jaffe (1996). Dominant chemical reactions controlling the redox are shown. The solid line corresponds to the average sediment, and the dotted line corresponds to sediment subject to significant bioturbation.

SCENARIOS MODELLED

The following chemical scenarios were considered.

- Resuspension of sediment into water of existing quality (as measured on the sampling trip). This is also equivalent to infiltration of overlying water of current quality into sediment by hydraulic head.
- Infiltration of surface water into sediment of quality represented by extremes of pH historically observed.
- Movement of the redox profile due to bioturbation or input/decrease of carbon.
- Significant elevation of redox by exposure to atmospheric oxygen.

These scenarios were all superimposed on the following calculated Eh-pH diagrams.

Eh-pH PREDOMINANCE DIAGRAMS OF SELECTED RADIONUCLIDES

The average water derived from “Water Quality on Disk” was input into the chemical speciation model, with concentrations of radionuclides taken from the DWAF (1996) report. The radionuclides considered were isotopes of uranium, thorium, radium and lead. There is not sufficient published thermodynamic data for the modelling of the speciation of polonium.

The values of pH and oxidation potential (Eh) were scanned across values that are typical of fresh water sediments. The dominant chemical species of the radionuclides were identified, and diagrammed as a function of pH and Eh. This type of diagram is called a Pourbaix diagram.

The lines on the Eh-pH predominance diagram correspond to equal concentrations of the dominant chemical species diagrammed in the sectors of the diagram

In the case of uranium, a number of different possible solids exist in the high redox and alkaline region. The selective precipitation of the solids was modelled. The case where no precipitate emerges was also modelled. This is the short-term condition of the system.

On the following predominance diagrams, surface water sites (2-10) are located in terms of measured Eh and pH (Appendix 7). The point corresponding to site 1 is absent from the Eh-pH diagrams, because the site was dry at the time of sampling.

Letters A to D signify theoretical redox conditions at different sediment depths. Dotted lines E and F refer to observed extremes of pH in the environment.

Concentrations of radionuclides modelled were required to be close to those observed in the environment. The maxima of the water-column concentrations of the radionuclides were obtained from the database of measurements referred to in the DWAF report on the Radioactivity Monitoring Programme in the Mooi River Catchment (DWAF, 1999). The concentrations, in Table 2, were used in the chemical speciation calculations to generate the Eh-pH diagrams (Figures 10 to 16). The concentration of radium was set at 0.01 µM.

Table 2 Maxima of normal solution concentrations of selected radionuclides

Radionuclide	U-238	U-234	Th-230	Pb-210	Po-210	U-235	Th-227	Th-232
ppm	2.84x10^{-1}	1.53 x10^{-5}	1.91 x10^{-8}	3.48 x10^{-11}	3.61 x10^{-14}	2.24 x10^{-3}	3.47 x10^{-14}	2.34 x10^{-3}
mBq/L	3513.1	3470.0	13.7	112.9	6.4	178.7	40.6	9.6
mol/L	1.19 x10^{-6}	6.56 x10^{-11}	8.28 x10^{-14}	1.66 x10^{-16}	1.72 x10^{-19}	9.55 x10^{-9}	1.53 x10^{-19}	1.01 x10^{-8}

Eh-pH Diagrams of Uranium

Figures 10 through 12 feature the chemical speciation of Uranium under the conditions corresponding to the scenarios selected above.

The diagrams in this section correspond to differing assumptions regarding the rates of precipitation of the uranium species at high alkalinity.

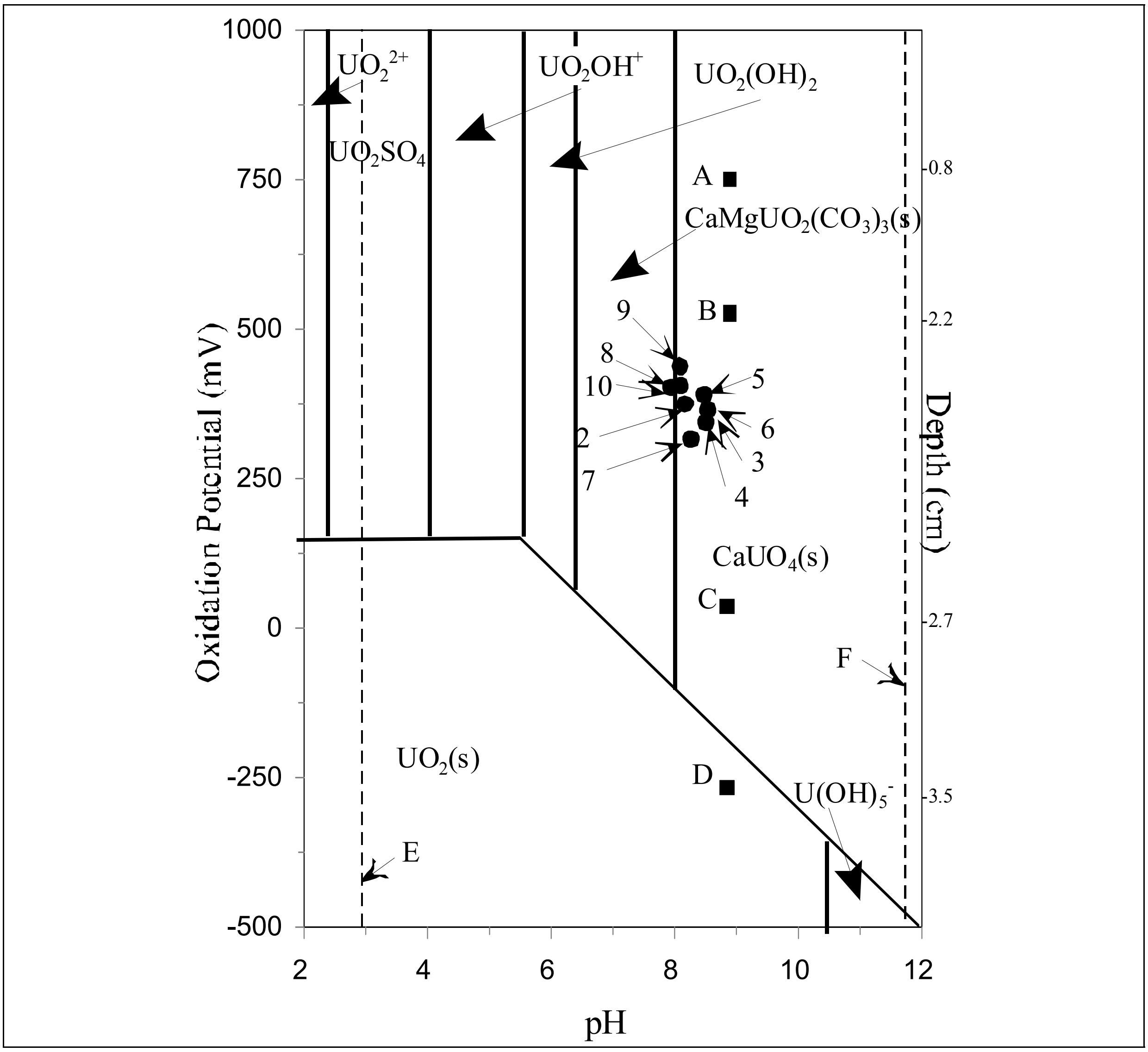


Figure 10 Eh-pH diagram of the fate of 1.19µM uranium in the average Mooi river water, with calcium uranate and calcium magnesium uranyl carbonate allowed to precipitate. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment

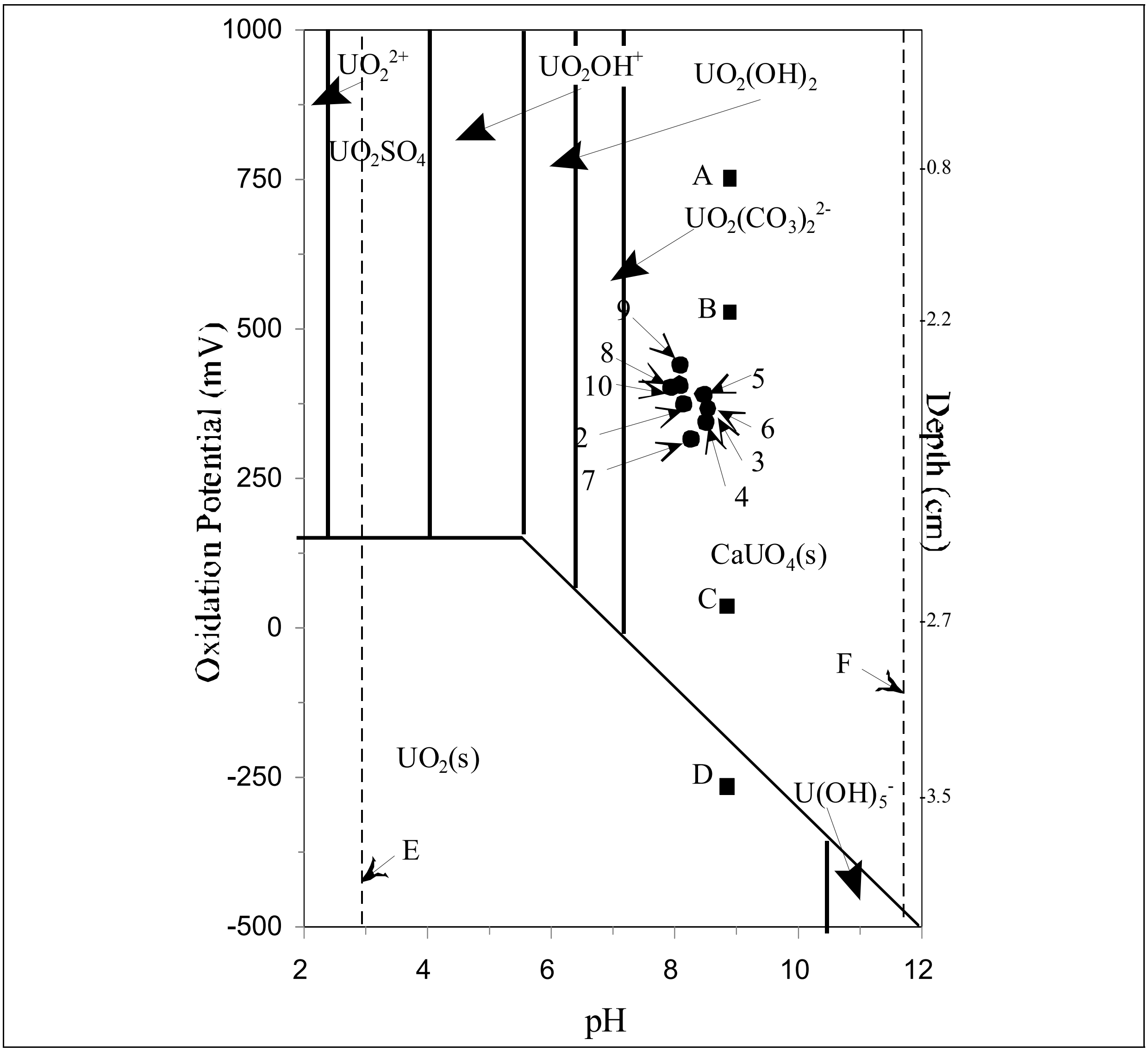


Figure 11 Eh-pH diagram of the fate of 1.19 µM uranium in the average Mooi river water, with calcium uranate allowed to precipitate. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment

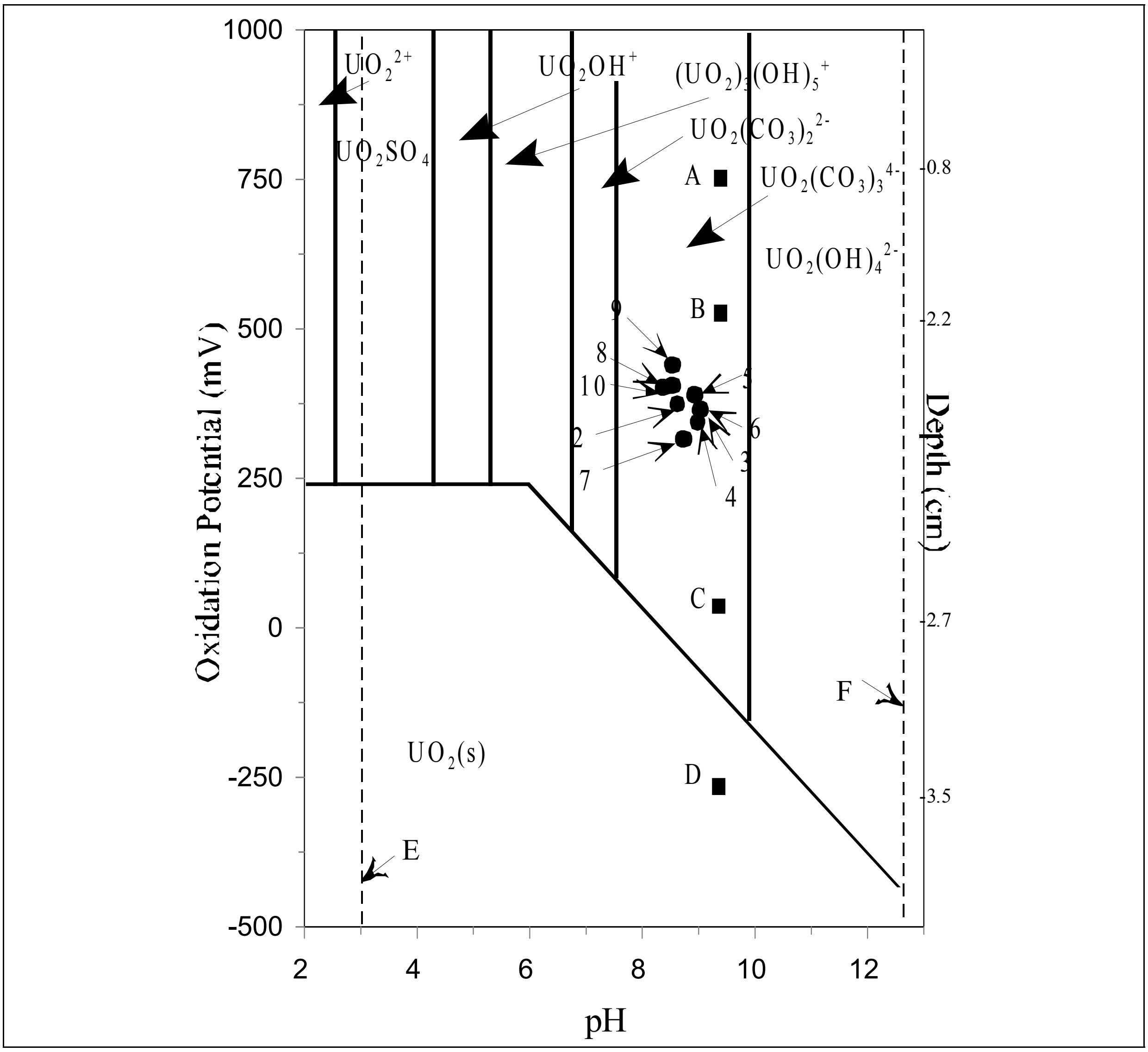


Figure 12 Eh-pH diagram of the fate of 1.19 μM uranium in the average Mooi river water, with neither calcium uranate nor calcium magnesium uranyl carbonate allowed to precipitate. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment

Eh-pH Diagram of Thorium

Figure 13 features the chemical speciation of thorium under the conditions corresponding to the scenarios selected above.

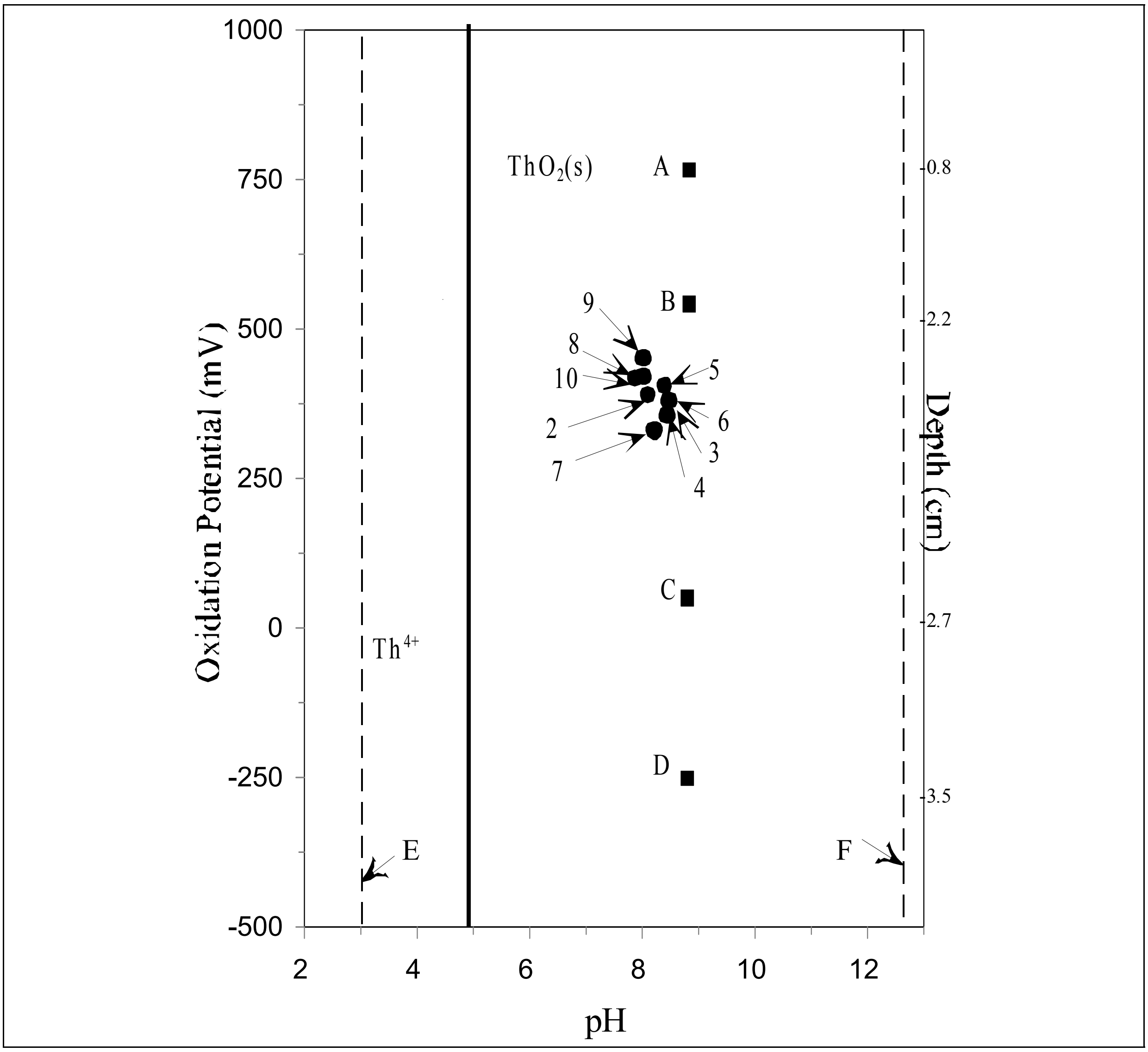


Figure 13 Eh-pH diagram of the fate of 0.01 µM thorium in the average Mooi river water. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment.

Eh-pH Diagram of Radium

Figure 14 features the chemical speciation of radium under the conditions corresponding to the scenarios selected above.

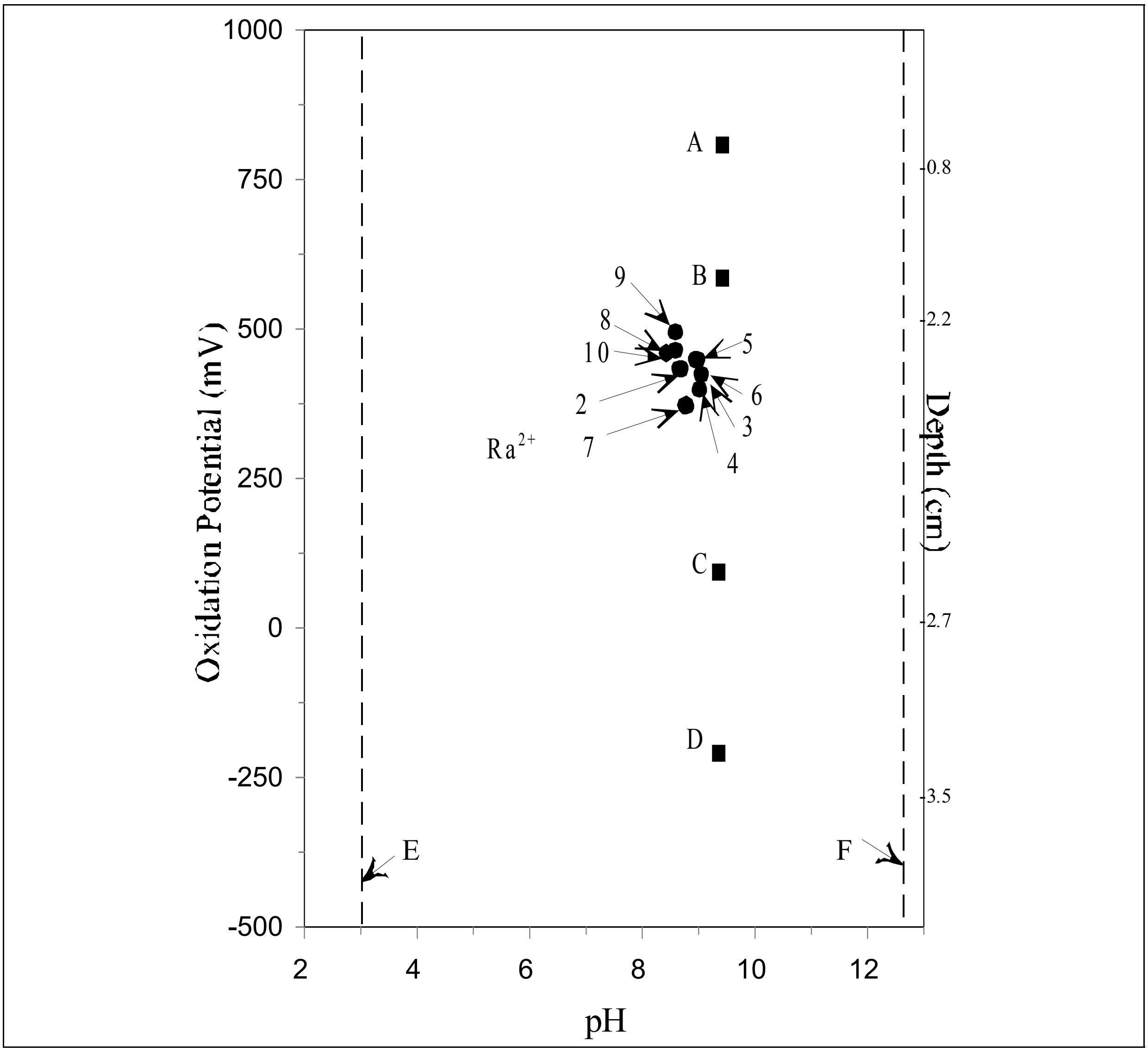


Figure 14 Eh-pH diagram of the fate of 0.01 µM radium in the average Mooi river water. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment.

Eh-pH Diagram of Polonium

Figure 15 features the chemical speciation of polonium under the conditions corresponding to the scenarios selected above.

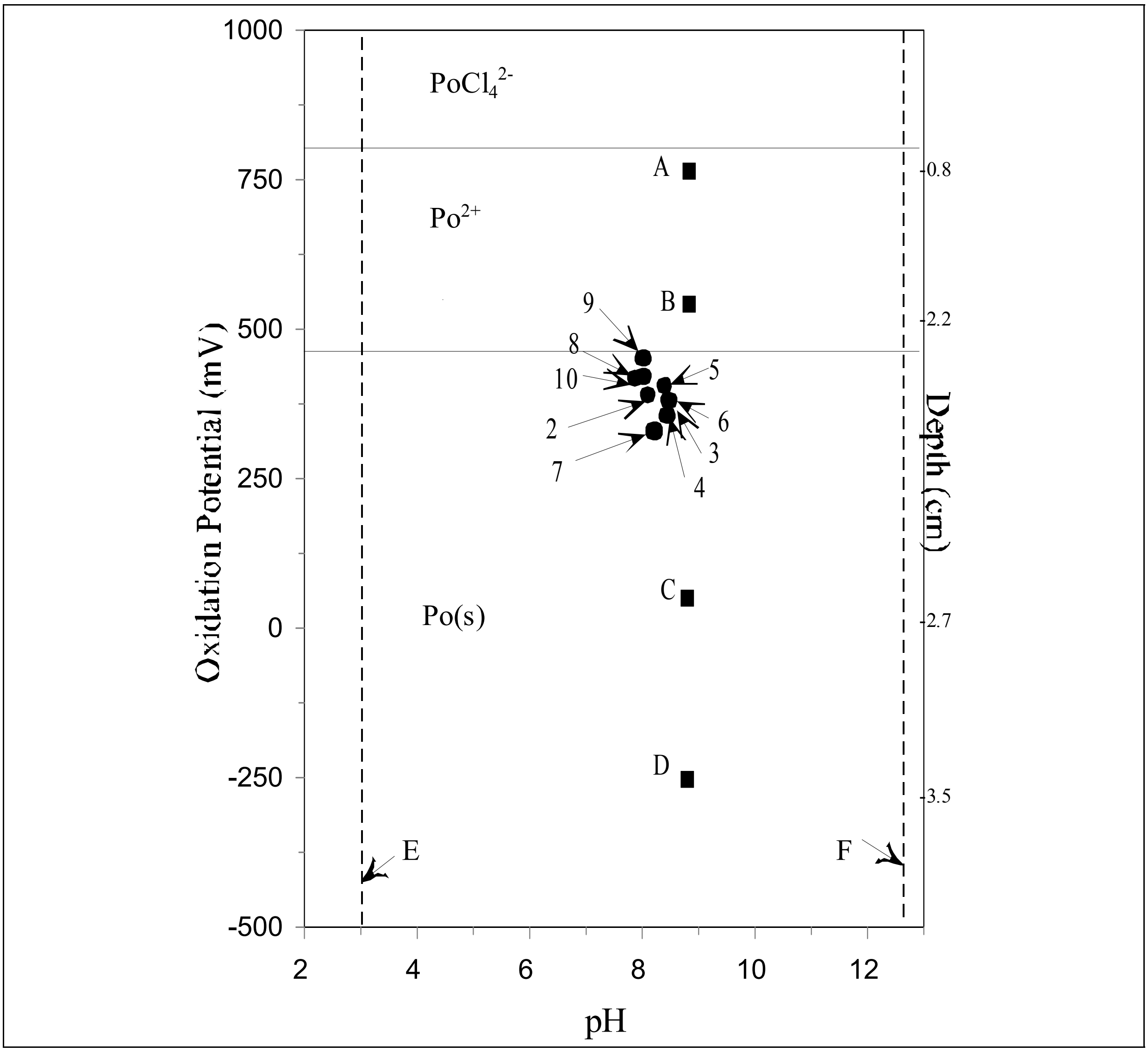


Figure 15 Eh-pH diagram of the fate of $1x10^{-19}$ M polonium in the average Mooi river water. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment.

Eh-pH Diagram of Lead

Figure 16 features the chemical speciation of lead under the conditions corresponding to the scenarios selected above.

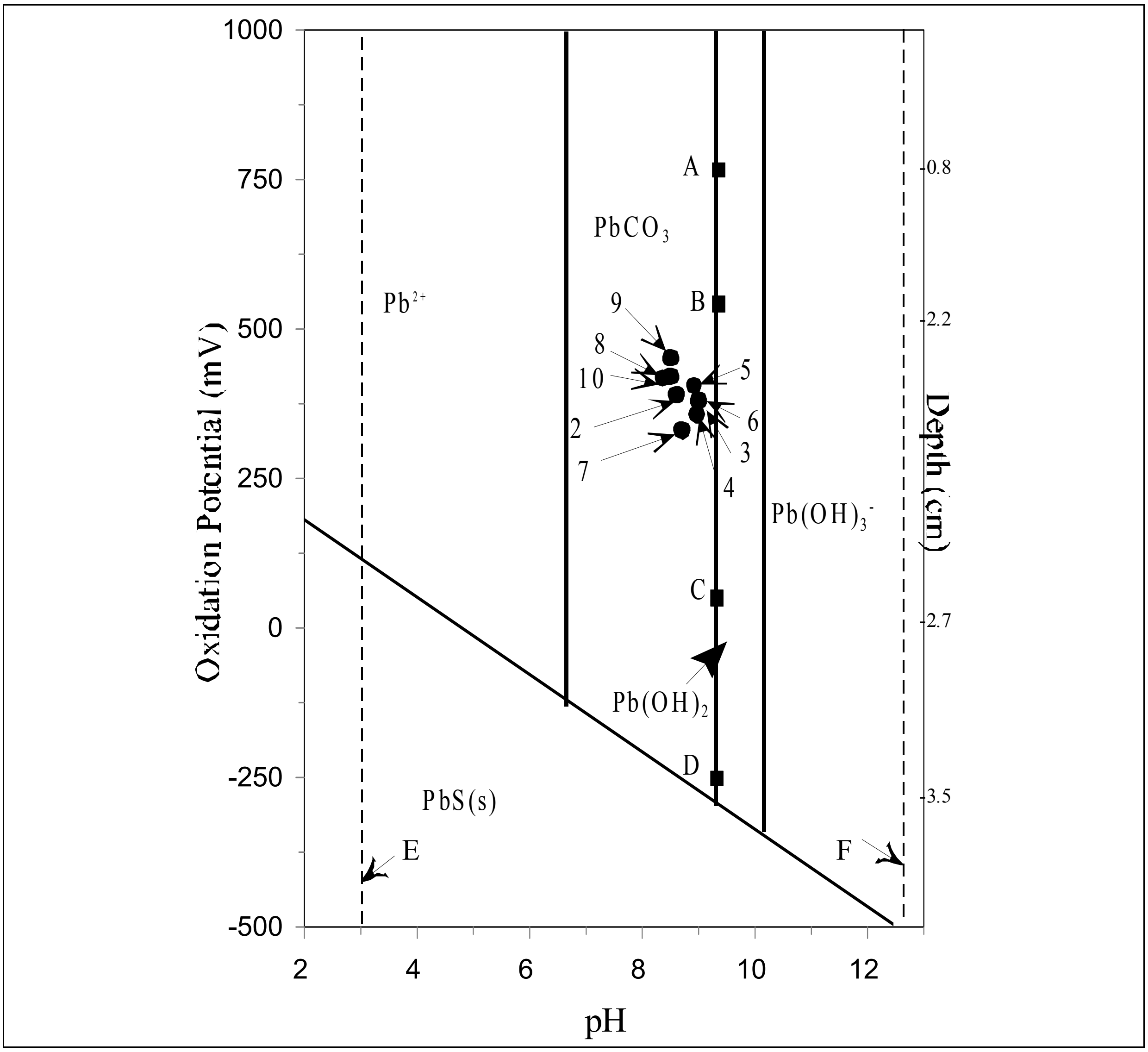


Figure 16 Eh-pH diagram of the fate of $1x10^{-16}$ M lead in the average Mooi river water. Surface water at sites are numbered from 2 to 10. Letters A-D signify theoretical redox conditions at different sediment depths. Dotted lines E and F correspond to observed extremes of pH in the catchment.

EVALUATION OF SCENARIOS WITH RESPECT TO RADIONUCLIDE MOBILITY

The assumption maintained throughout this section is that if the radionuclides are in a soluble form, they are capable of being transported by the water column, and if they are in a solid form, they are likely to flocculate or deposit by sedimentation, and are relatively immobile.

Scenario 1: Resuspension (e.g by turbulence) of sediment into water of existing quality (as measured July, 1999)

This scenario corresponds to the points in Figures 10 to 16, depicted by the solid circles, and labelled 2 through 10.

Fate of Uranium

Figures 10 to 12 refer. Under the prevailing redox and pH conditions of the surface water, uranium is expected to be in the solid form as $CaMgUO_2(CO_3)_{3(s)}$, or as $CaUO_{4(s)}$. If the former solid doesn't form, and the latter forms (Figure 10), uranium is expected to be insoluble. If neither solid forms in the short term (Figure 11), uranium will be solubilized in the form of a uranyl carbonate.

Fate of Thorium

Figure 13 refers. Thorium is in the form of ThO_2, which is insoluble at the 0.01μM levels.

Fate of Radium

Figure 14 refers. Radium is entirely soluble at a concentration of 0.01μM.

Fate of Polonium

Figure 15 refers. Polonium is predominantly in the form of the solid metal, but exists in the soluble cationic form at redox levels higher than that of the river waters.

Fate of Lead

Figure 16 refers. Lead is predominantly in the form of the soluble carbonate complex under the conditions of the overlying water, and is expected to be mobilised.

Scenario 2: Infiltration of surface water at extremes of recorded pH values

This scenario corresponds to the dotted vertical lines in Figures 10 to 16, labelled E and F.

The redox potential of the sediments of the Mooi River catchment seem to be controlled by reduction of ferric ion and of sulphate.

If the dominant environmental redox couples remain largely unaltered by the pH change, this scenario represents the redox zone between the points C and D in the diagrams.

Fate of Uranium

Figures 10 to 12 refer. At the extreme of low pH, uranium is expected to be immobilised as uraninite, $UO_{2(s)}$. At higher pH, if $CaMgUO_2(CO_3)_{3(s)}$, or $CaUO_{4(s)}$ are formed, then uranium will be immobilised as the solid. If neither solid forms in the short term (Figure 11), uranium will be solubilized in the form of a uranyl carbonate or hydroxide above a pH of about 9.

Fate of Thorium

Figure 13 refers. At high and intermediate pH, thorium is in the form of ThO_2, which is insoluble at the 0.01µM level. At the extreme of low pH, thorium may exist in the soluble ionic form, or as the soluble sulphate complex.

Fate of Radium

Figure 14 refers. Radium is entirely soluble at a concentration of 0.01µM.

Fate of Polonium

Figure 15 refers. Polonium remains unaffected by this environmental modification.

Fate of Lead

Figure 16 refers. In acid conditions, lead is immobilised as the sulphide. In neutral and alkali pH conditions, lead may exist as the sulphide, or may be soluble as the solution carbonate complex, or as the hydroxide complex, and is thus expected to be mobilised.

Scenario 3: Movement of the redox profile due to bioturbation or input/decrease of carbon

Figure 8 shows the theoretical (modelled) depth of the zones of redox potential, as controlled by the relevant dominant reduction reactions. The sediments of the study area seem to be controlled by reduction of ferric ion and sulphate.

The depth of the redox zones is little affected by normal changes in sedimentation of organic matter.

At the limit of expected bioturbation, the redox zone controlled by sulphide moves from about 3.5cm depth to about 5 cm depth. That of ferric moves down by a similar amount, but the depth at which the other reactions are expected to occur does not change much.

This scenario represents movement of the redox zone from point C to D in Figures 10 to 16.

Fate of Uranium

Figures 10 to 12 refer. At pH less than 9, uranium is expected to be immobilised as uraninite, $UO_{2(s)}$. If $CaMgUO_2(CO_3)_{3(s)}$, or $CaUO_{4(s)}$ are formed, then uranium will be immobilised as the solid throughout the expected pH range. If not, then uranium will possibly remain in solution as the carbonate.

Fate of Thorium

Figure 13 refers. At all pH values, thorium is immobilised in the form of ThO_2, which is insoluble at the 0.01µM level.

Fate of Radium

Figure 14 refers. Radium is entirely soluble at a concentration of 0.01µM.

Fate of Polonium

Figure 15 refers. Polonium remains unaffected by this environmental modification.

Fate of Lead

Figure 16 refers. In acid conditions, lead is immobilised as the sulphide. In neutral and alkali pH conditions, lead may exist as the sulphide, or may be soluble as the solution carbonate complex, or as the hydroxide complex, and is thus expected to be mobilised. As the redox is decreased from point C to D, lead becomes insoluble at higher and higher pH values.

Scenario 4: Significant elevation of the redox profile by exposure to atmospheric oxygen.

The redox level of atmospheric oxygen is near the point A on Figures 10 to 16. The pH is usually affected by increase in oxidation potential, as oxidation of ferrous ion and sulphide is accompanied by concomitant release of protons. The Mooi River catchment has a significant concentration of dolomite, however, and the pH is thus expected to range from 2 (acid rock drainage) to 10 (equilibrium with calcite).

Fate of Uranium

Figures 10 to 12 refer. If $CaMgUO_2(CO_3)_{3(s)}$ is formed, uranium will be soluble below pH 6.5. If only $CaUO_{4(s)}$ is formed, then uranium will be soluble below pH 7 (Figure 10). If neither are formed, then uranium will be totally soluble in the entire expected pH range.

Fate of Thorium

Figure 13 refers. At all pH values, thorium is immobilised in the form of ThO_2, which is insoluble at the $0.01\mu M$ level.

Fate of Radium

Figure 14 refers. Radium is entirely soluble at a concentration of $0.01\mu M$.

Fate of Polonium

Figure 15 refers. Polonium exists in the soluble cationic form at this redox level.

Fate of Lead

Figure 16 refers. In alkaline conditions, lead may be immobilised as the tetraoxide. In all other pH conditions, lead is soluble as the solution carbonate complex, or as the free ion.

WHAT DO THE FIELD GAMMA MEASUREMENTS TELL US?

Measurements in counts per second (cps) are shown in the following graphs.

The concentrations of radionuclides are expressed as ppm (parts per million = mg/kg dry weight).

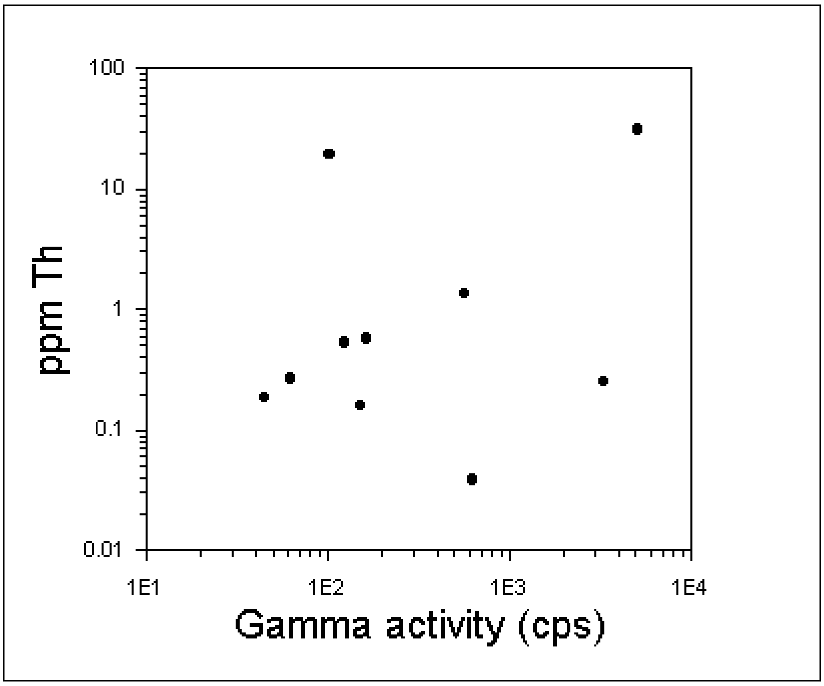


Figure 17 Measured Thorium-232 (ppm) as a function of field gamma activity

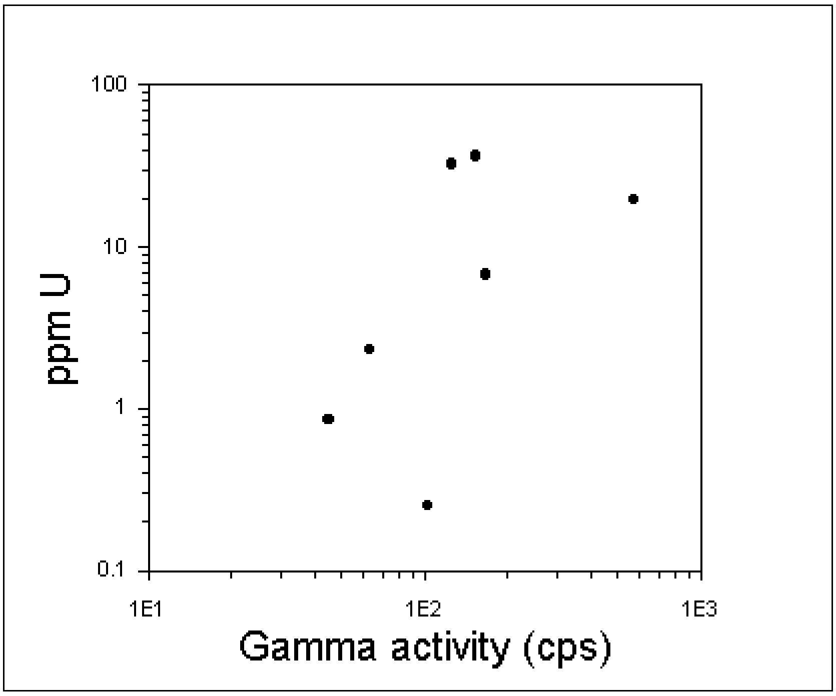


Figure 18 Measured Uranium-238 (ppm) as a function of field gamma activity

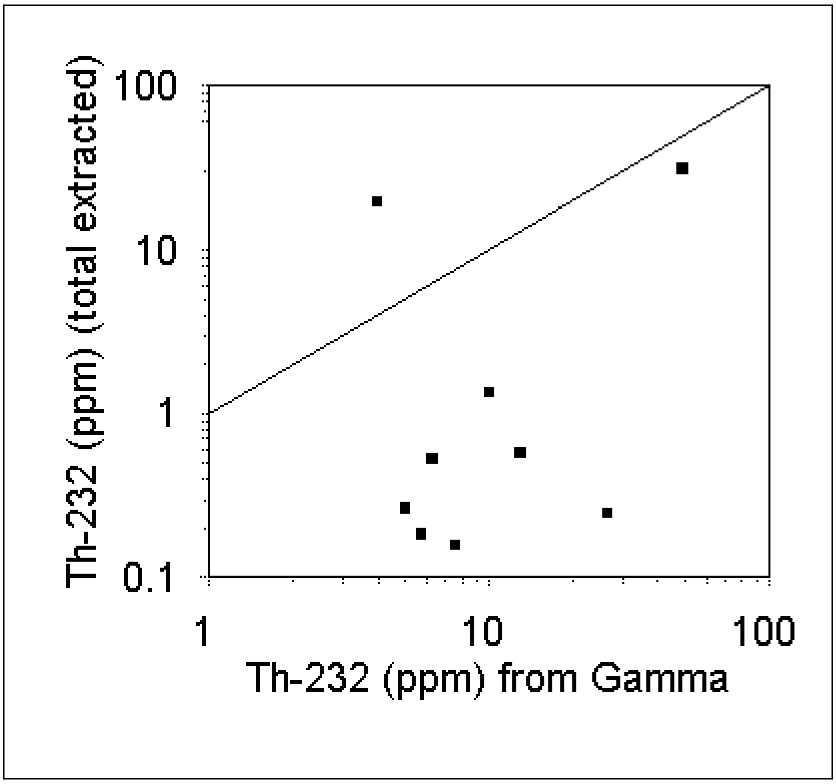


Figure 19 Deviation of measured Th-232 (ppm) from that calculated from gamma measurements, assuming equilibrium with low-end daughters.

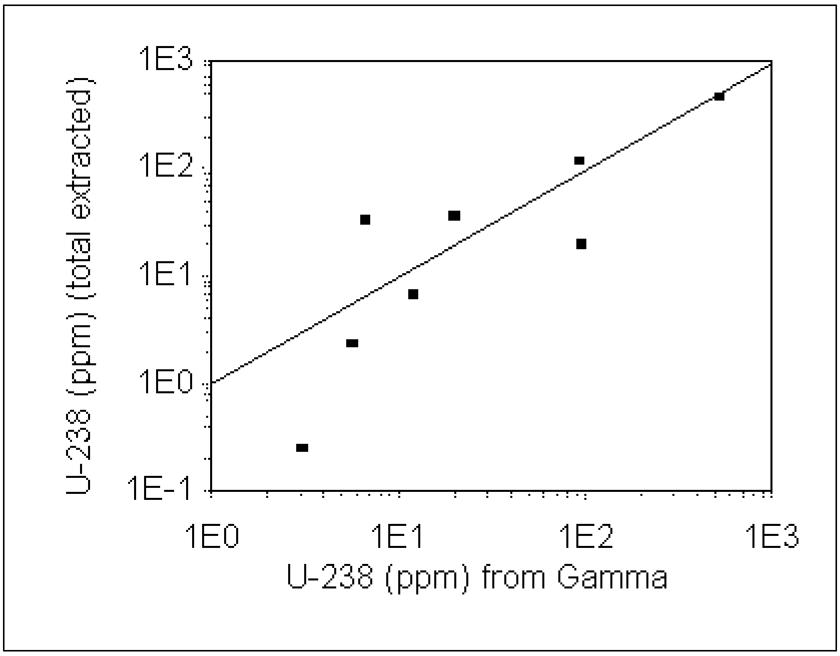


Figure 20 **Deviation of measured U-238 (ppm) from that calculated from gamma measurements, assuming equilibrium with low-end daughters.**

FIELD GAMMA MEASUREMENTS - PROXY FOR WHAT RADIONUCLIDES?

Figure 17 shows the measured Th-232 concentration as a function of gamma intensity. There is no persuasive correlation between the measurements. This may indicate that the gamma intensity is not a good proxy for the Th-232 concentration in the sediments.

There is also the possibility that the field gamma detector identifies Th-232 in the field, which is not subsequently stripped from the sediments in the sequential chemical extraction phase. Thorium oxide is very refractory, and may well report in the residual or inert fraction of the sequential chemical extracts, which were not included in this study.

This possibility is given some weight upon consideration of Figure 19 in which the Th-232 concentration (in ppm) observed in the sequential chemical extractions is compared with that predicted from the field gamma measurements.

All reliable Th-232 data measured by inference in the field gamma spectrum are higher than those extracted chemically. However, there is still no significant correlation between extractable and gamma-indicated Th-232.

There is a higher apparent correlation of total U-238 extracted from the sediments, and the field gamma intensity (Figure 18). The plot of total extractable U-238 versus U-238 derived from gamma intensity of daughter products (Figure 20) exhibits a high correlation between these entities.

The field gamma intensity is thus a fair proxy of U-238 concentration in the environment. It is noted that the lower the concentration of uranium, the greater the deviation from exact prediction by gamma radiation, assuming secular equilibrium, and 2π irradiation of the gamma detector.

WHAT DO THE SEQUENTIAL EXTRACTIONS TELL US?

HAS URANIUM ACCUMULATED IN THE SEDIMENT?

The following figure illustrates the relative amounts of uranium stored in the sediments (as total liberated from the sequential extraction procedures) compared to that in the solution column. The solution uranium concentration was taken as similar to the average of those determined in the DWAF study of 1997 (DWAF, 1999).

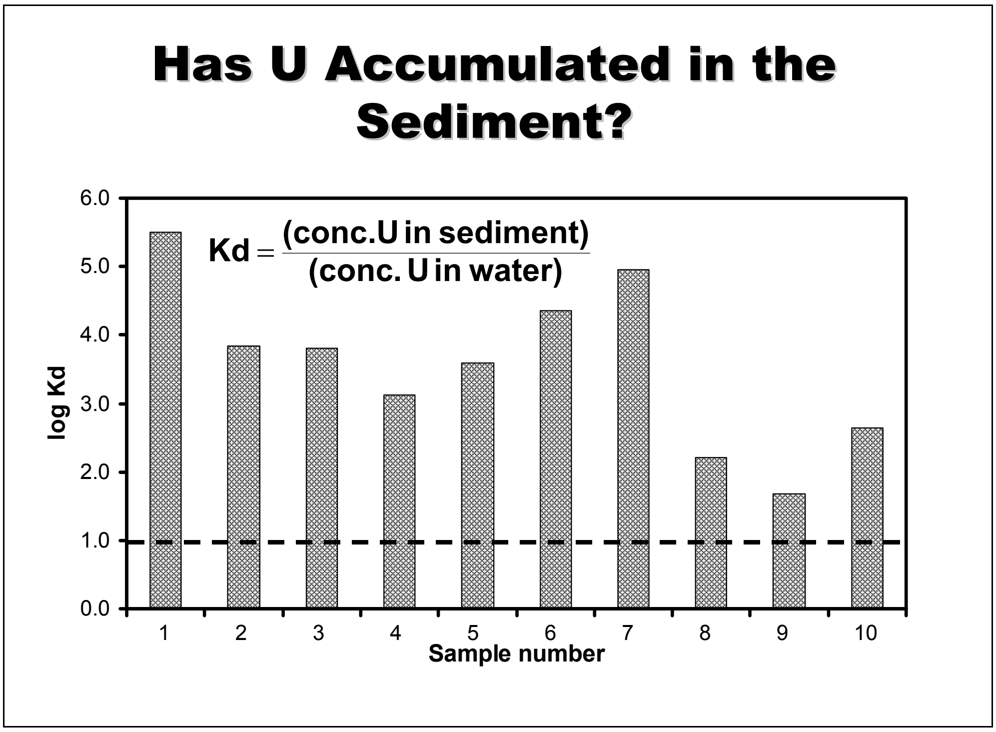


Figure 21 Partition coefficients (Log Kd) for uranium between sediment and water phases. The aqueous U concentration was taken from the DWAF study of 1997.

ANALYSIS BY PHASE OF SEQUENTIAL EXTRACTION

Figure 22 shows the U-238 activity (Bq/kg) measured for each step in the sequential extraction process. The steps correspond to the following operations:

Sequential Extraction Step	Conditions of extraction	Possible Environmental Phases
Step 1	Loosely bound metal (easily extractable)	Clays, weak adsorption sites in Iron and Manganese oxyhydroxides
Step 2	Mild acid exchangeable	Carbonates
Step 3	Reducing conditions	Iron and Manganese oxyhydroxides
Step 4	Oxidising conditions	Organic carbon and sulphide

It can be seen that the uranium extracted in each fraction is largely unmobilised in the easily extractable fraction.

The bulk of the uranium seems in the majority of the samples to be solubilised in weak acid. The pH of waters in the catchment have sometimes been as low as 3 in recorded history

There is still an appreciable fraction of uranium retained in the fraction solubilised under reducing conditions, and there is still some uranium in the phase that is oxidised.

Thus, it can be seen that uranium can be released in any of the environmental extremes expected to occur.

These observations are depicted graphically in the following section:

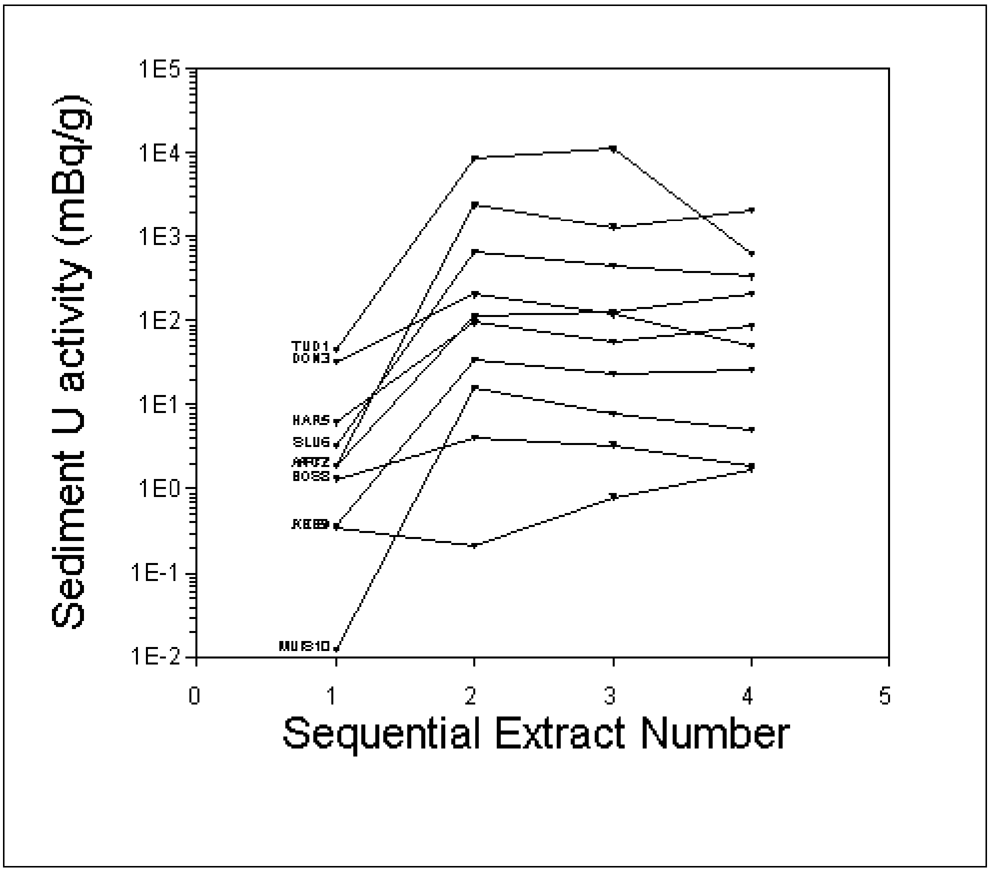


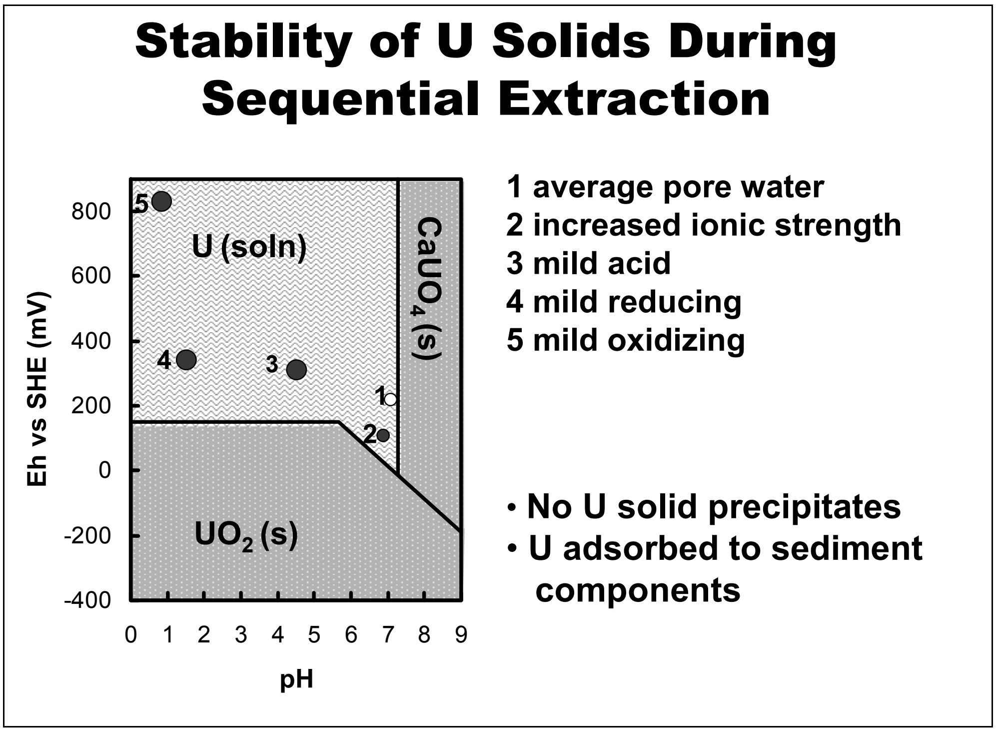
Figure 22 U-238 activity (Bq/kg) measured for each step in the sequential extraction process. Step 1 corresponds to loosely bound metal, Step 2 to mild acid exchangeable, Step 3 to reducing conditions and Step 4 to oxidising conditions.

CHEMICAL FORM OF URANIUM IN SEDIMENTS - ANALYSIS OF RELATIVE QUANTITIES OF URANIUM EXTRACTED BY EH-PH DIAGRAMS:

Does released U come from precipitated Uranium solids?

One hypothesis of uranium deposition in the sediments studied is that uranium is deposited as a solid, possibly as an oxide or as calcium uranate.

The following diagram shows the stability of uranium solids during sequential chemical extractions.



Stability of U Solids During Sequential Extraction

1 average pore water
2 increased ionic strength
3 mild acid
4 mild reducing
5 mild oxidizing

- No U solid precipitates
- U adsorbed to sediment components

Figure 23 Test of the hypothesis that uranium extracted from the sediments originates from a uranium solid. Point numbers on the Eh-pH diagram refer to the conditions of the extraction steps. Size of markers associated with the numbers is relative to the amount of uranium extracted. The open circle at condition 1 means insignificant extraction of uranium

As may be seen in the above figure, all conditions in the sequential extractions correspond to uranium in the solution phase.

Pore water conditions are such that no U solid is expected to precipitate.

The fact that uranium is extracted at all steps above that corresponding to pore water conditions means that uranium from different phases is being sequentially extracted, and that the uranium is not being extracted from a solid uranium mineral phase.

Does released U come from environmental solid phases?

The following diagram probes the possibility that uranium is extracted from environmental phases that it is adsorbed to in the natural sediment conditions.

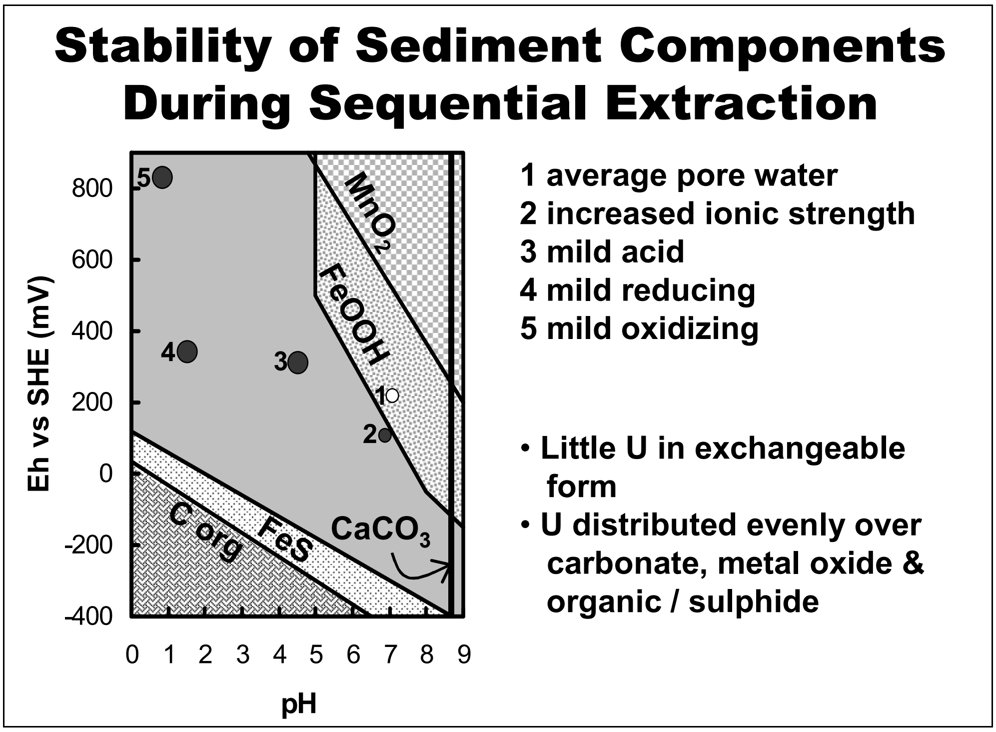


Figure 24 Test of the hypothesis that uranium extracted originates from the environmental phases expected in the core samples of sediment. Point numbers on the Eh-pH diagram refer to the conditions of the extraction steps. Size of markers associated with the numbers is relative to the amount of uranium extracted. The open circle at condition 1 means insignificant extraction of uranium from the sediment.

The figure above indicates the stability domains of the environmental phases expected to exist in the sediment. Superimposed are the conditions of the sequential extraction process, and the amount extracted per step.

Pore water (point 1) is in the domain of stability of iron hydroxides. Thus, it might be imagined that uranium may adsorb to iron oxides present.

When conditions are moved outside the zone of stability of iron hydroxides (point 2), some uranium is released, suggesting that this is the case.

However, not all the uranium is desorbed in this step. When the conditions are changed, to favour the rapid dissolution of environmental carbonates (point 3), some uranium is released. This uranium may exist as a U carbonate, or be included in a calcite phase.

When conditions are modified to favour the rapid dissolution of iron and manganese oxides, (point 4), more uranium is released. This U may well be bound by Fe and Mn oxyhydroxides.

Finally, when conditions are modified to favour rapid dissolution of organics or sulphides, more U is released from the sediment. It is considered more probable that this U fraction is bound to organics than to sulphides in the sediment.

ANALYSIS BY TOTAL U-238 AT EACH SITE

Figure 25 shows the total extractable U-238 at each site, and the U-238 found by measurement of field gamma spectra (with the assumption of secular equilibrium). The sites TUD1 - MUIS10 are arranged according to the order downstream from the source of the river. Site BOS8 is the Boskop Dam, and KKD9 is the Klerkskraal Dam, which is the control in this study.

Relative concentrations of U-238 at each site are depicted in Figure 3.

The U-238 concentration predicted from the field gamma measurements is really an indication of the concentration of daughter products by comparison to the parent. If there are more daughter products than the parent U-238, which would occur if the U-238 is selectively leached from a system by environmental conditions that leave the daughters immobilised, then one would expect the U-238 predicted from the gamma measurements to be higher than that found by chemical extraction.

Using this argument, the sites containing elevated levels of uranium all have measured U-238 higher than that predicted based on the gamma-emitting daughters. This implies that U-238 has been injected into the system at a higher rate than that required for secular equilibrium to form.

A significant anomaly exists at Harry’s Dam, where it seems that parent U-238 is depleted by comparison to the daughters. This could indicate a selective leaching event at this dam. However, in the linear plot of specific activity versus site ordination in Figure 26, the differences between the concentrations measured by gamma spectrometry and by chemical extraction could be viewed as slight.

The trends in concentration of U-238 downstream indicate a possible strong source of U-238 in Tudor Dam (TUD1), with subsequent dilution along the river, down to Harry’s Dam (HAR5).

Abe Bailey Dam (ABE4) is slightly off the main stream, and exhibits low U-238 by comparison with that of the main channel.

There is mine water input at the Sluice (SLU6), which results in elevated U-238 by comparison to that of Harry’s Dam, but not at all as high as the concentrations in Andre Coetzee’s Dam (A-C7). This indicates that U-238 might be emitted in a mobile form, which is accumulating in the strongly reducing environment in Andre Coetzee’s Dam

The concentration of U-238 drops from Andre Coetzee’s dam to Muiskraal (MUIS10), which has U-238 activity higher than the Boskop Dam (BOS8). The Boskop Dam has U-238 activity higher than the control, Klerkskraal Dam (KKD9).

The latter observation suggests a scenario of great accumulation of U-238 in Andre Coetzee’s dam, with some slight migration down to Muiskraal (MUIS10), and some migration into the Boskop Dam (BOS8), to elevate the U-238 content above that of Klerkskraal Dam. However, again, reference to Figure 27 suggests that the activities in the latter measured sediments is relatively slight, by comparison with the more radioactive sediments upstream.

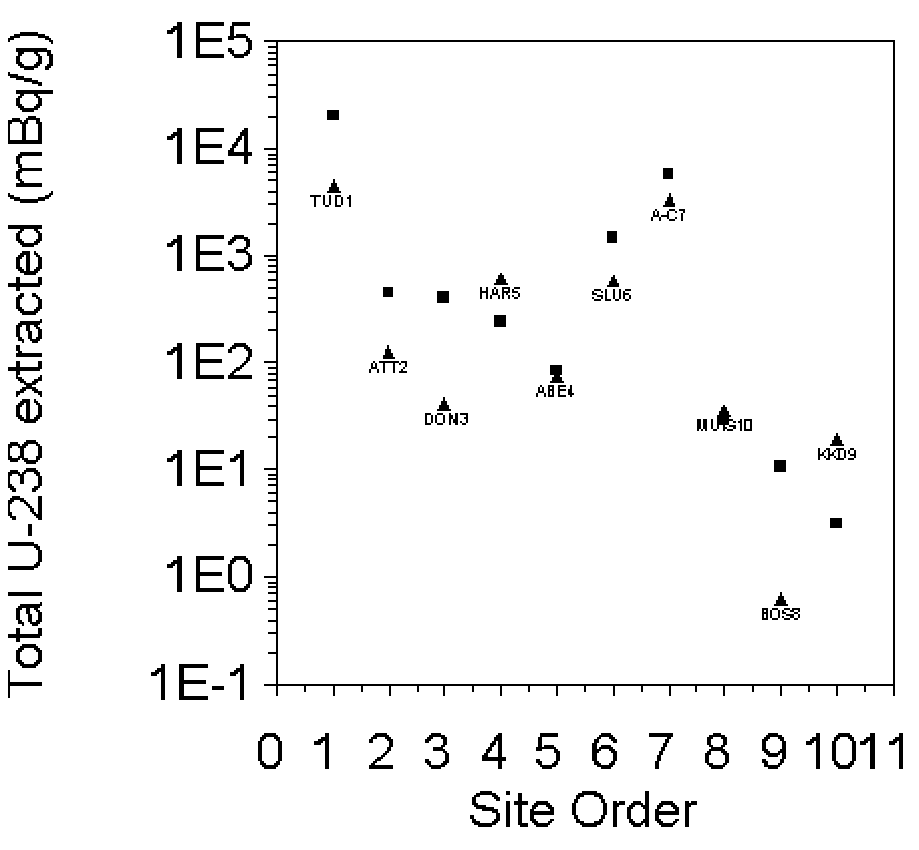


Figure 25 **Total Bq/kg U-238 extracted (squares) and total Bq/kg U-238 predicted from gamma measurements of low-end daughters (triangles). Activity is plotted on a log scale. Disequilibrium is identified by the distance between the squares and the triangles. The Nuclear Energy Act of 1993 stipulates unconditional deregulation only for sites below 200 Bq/kg.**

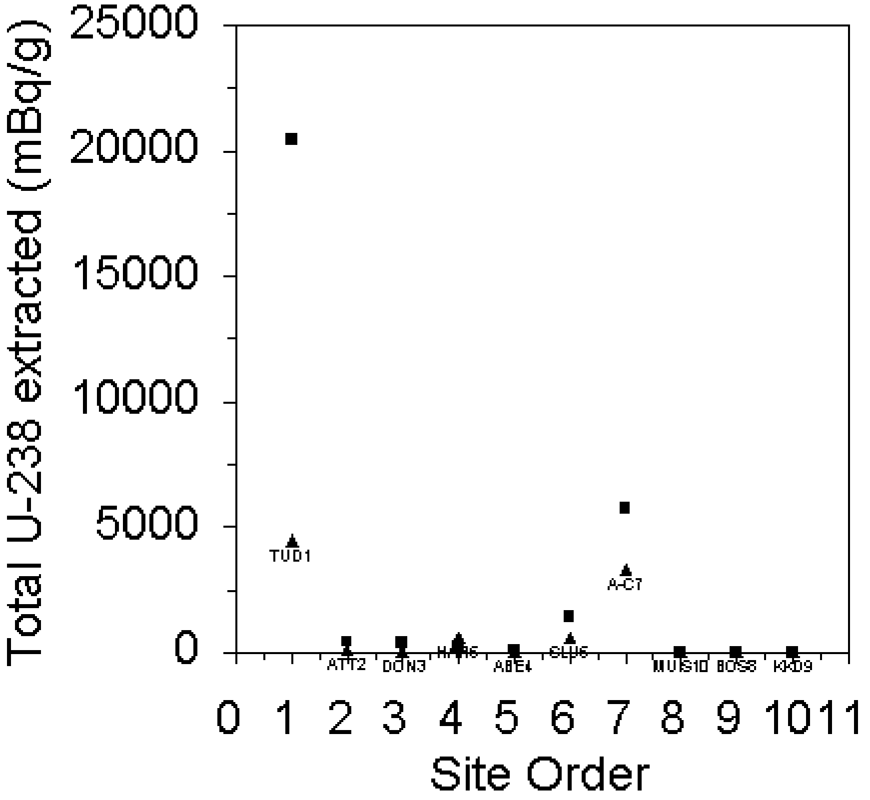


Figure 26 Total Bq/kg U-238 extracted (squares) and total Bq/kg U-238 predicted from gamma measurements of low-end daughters (triangles). Activity is plotted on a linear scale. The Nuclear Energy Act of 1993 stipulates unconditional deregulation only for sites below 200 Bq/kg.

SECULAR DISEQUILIBRIUM AS INVESTIGATED BY RATIOS OF SEDIMENT RADIONUCLIDE ACTIVITIES

The activity ratios are presented in Appendix 11.

Origin of Uranium in The Sediments

The U-238/U-235 ratio is always close to 21.7, meaning that there has been no artificial tampering with the natural ratio of the radionuclides by extraction of U-235. The uranium is therefore of natural origin.

The U-238/U-234 ratio of all the significant measurements in the sample extracts is very close to 1.0, meaning that the uranium extracted from the river sediments originates in recently crushed rock as would occur in a mining operation.

Disequilibrium - Enrichment or depletion ?

The U-234/Ra-226 ratio indicates whether uranium has been input into an environmental system at a rate greater than the rate of secular equilibration of the radionuclides. In most cases, where measurements were significant, there is an enrichment of U-234 over Ra-226.

Possible Age of Disequilibrium Processes

The Ra-226/Pb-210 ratio tells us the short-term age of the disequilibrium processes from the top end of the decay series to the bottom. The more contaminated the sediments, the greater the excess of Ra-226.

RISK ASSESSMENT

SCENARIO EVALUATION

Scenarios Simulated by Chemical Equilibrium Modelling

In all scenarios considered, there was the possibility of uranium being solubilized by environmental processes that fall within the bounds of reason. The scenario under which uranium is least likely to be mobilised is that of strongly reducing environmental conditions.

The scenario under which uranium is most likely to be solubilized is that of high oxidation potential and low- to intermediate pH. This scenario is likely if the sediments of an impoundment are exposed by drainage, or by dredging operations. Increased oxidation potential automatically enhances the potential for low pH conditions.

Thorium is expected to remain in the chemically inert fraction, and transport of thorium is most likely to be as a particulate with comparatively limited migration potential.

Scenarios Simulated by Sequential Chemical Extraction

In all of the sediments tested, uranium was mobilised by reaction with weak acid. Uranium was also mobilised by increase in oxidation potential, and by decrease in oxidation potential.

Thorium was not expected to be extracted significantly in the extraction procedures. There is evidence that thorium remained in the inert fraction of the sediments.

Scenarios Observed in Field Site Assessments

There is evidence that uranium is transported in a soluble form along the length of the Wonderfontein Spruit and Mooi Rivier Loop. Uranium is input at defined sources, e.g. Tudor Dam and the Sluice, and it reports at localities downstream where one would not expect particulates to reach (i.e. they may be filtered by reed beds).

There is evidence that uranium is transported from the Sluice into Andre Coetzee’s dam, where it is currently largely immobilised, or stored, by the low oxidation potential in the dam.

RISK QUOTIENT ESTIMATION

At the Tier I level, risk estimates such as the quotient method in the current application are used.

The exposure is represented by the environmental concentration of U-238, and the effect is represented by the 200 Bq/kg. limit stipulated by the Nuclear Energy Act of 1993 for unconditional deregulation of sites.

Figure 25 shows the U-238 activity at the sites along the Mooi River catchment, as measured by total chemical extraction.

Only the sediments corresponding to the Abe Bailey's Dam (ABE4), Muiskraal (MUIS10), Boskop Dam (BOS8), and the control, Klerkskraal Dam (KKD9) had uranium levels below the action level.

The sites Tudor Dam (TUD1), Attenuation Dam (ATT2), Donaldson Dam (DON3), Harry's Dam (HAR5), Sluice (SLU6) and Andre Coetzee's Dam (A-C7) had U-238 levels higher than the Nuclear Energy Act (1993) stipulation.

The latter sites therefore have a positive Tier 1 risk quotient, according to the equation:

$$RiskQuotient = \frac{Radioactive\ Concentration\ of\ Radionuclide}{Regulatory\ Exclusion\ Level\ for\ Radionuclide} = \frac{[{}^{238}U](Bq/kg)}{200\,Bq/kg}$$

The sites are ranked in order of increasing Tier 1 risk as follows:

Table 3 Sites Ranked by Tier 1 Risk Quotient

Highest Tier 1 Risk Quotient	Tudor Dam
	Andre Coetzee's Dam
	Sluice
	Attenuation Dam
	Donaldson Dam
Lowest Tier 1 Risk Quotient	Harry's Dam

CONCLUSIONS

The conclusions of the study may be graphically represented as in the following figure:

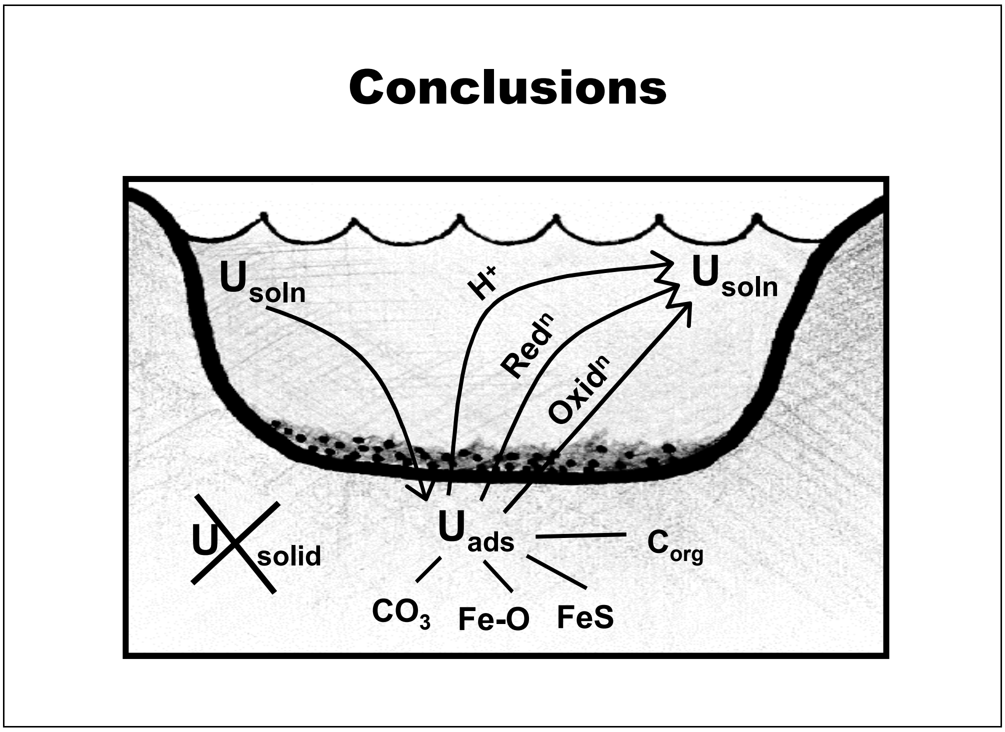


Figure 27 Conclusions of the study: Uranium has preferentially deposited in the sediments; the adsorbed Uranium may be desorbed into the solution phase by lowered pH, or by rapid changes in either reduction or oxidation potential.

The main aim of the study was to determine possible risks to humans of radionuclides in the sediments of the Mooi River catchment.

The study answered the research questions as follows:

- Radionuclides have been found to accumulate in the sediments of the Mooi River catchment.
- The main radionuclide of interest, being uranium, seems to be adsorbed to the environmental phases: carbonate, iron and manganese oxyhydroxides, and organics (with a slight possibility of being included in sulphide components).
- Uranium may be remobilised into the water column by perturbation of TDS, pH or oxidation potential.

The criterion for the Tier 1 Risk Assessment was the 200 Bq/kg limit stipulated by the Nuclear Energy Act of 1993 for unconditional deregulation of sites.

The sites Tudor Dam (TUD1), Attenuation Dam (ATT2), Donaldson Dam (DON3), Harry's Dam (HAR5), Sluice (SLU6) and Andre Coetzee's Dam (A-C7) had U-238 levels higher than the Nuclear Energy Act (1993) stipulation, and, therefore, had a positive Tier 1 Risk Quotient.

The sites are ranked in order of increasing Tier 1 risk as follows:

Table 4 Sites Ranked by Tier 1 Risk Quotient

Highest Tier 1 Risk Quotient	Tudor Dam
	Andre Coetzee's Dam
	Sluice
	Attenuation Dam
	Donaldson Dam
Lowest Tier 1 Risk Quotient	Harry's Dam

RECOMMENDATIONS

The objective of a Tier 1 Risk Assessment is to determine whether or not more detailed investigations are required.

Thus, it is recommended that a more detailed exposure assessment be conducted for the following impoundments, in the following order of risk:

Highest Tier 1 Risk Quotient	Tudor Dam
	Andre Coetzee's Dam
	Sluice
	Attenuation Dam
	Donaldson Dam
Lowest Tier 1 Risk Quotient	Harry's Dam

The chemical and hydro-dynamics of the catchment should be monitored over a year, in order to better model contaminant transport in the catchment.

A theoretical model of Potchefstroom's water treatment works should be constructed, to assess the ability of Potchefstroom to treat possible radionuclides flushing into the water source.

Considering the proximity of Andre Coetzee's Dam to the Boskop Dam, it is recommended that the extent of uranium deposition in Andre Coetzee's dam be assayed.

Uranium is immobilised in this dam by environmental processes that buffer the pH at a high level and the redox at a low level. The extent of this buffering capacity should be known in order to evaluate the risks of re-release of U-238 during possible dredging operations.

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APPENDIX 1: CHEMICAL ATTRIBUTES OF SEDIMENT COMPONENTS

This section focuses on the structural and metal-binding capacities of the various components of sediments.

GENERAL CHARACTERISTICS OF SEDIMENTS

Sediments are extremely heterogeneous substances, with a number of components mixed together, which are in intimate contact with each other, and which interact and exchange chemicals such as metal ions, inorganic anions and organic matter.

Broadly, sediments can be considered as containing the following components in differing proportions:

- Pore water
- Precipitates
- Solid organic matter
- Metal sulphides
- Occluded gases
- (Hydrous) oxides of iron, aluminium and manganese
- Clay minerals
- Aluminium silicates
- Calcite
- Sand (silica)
- Minor amorphous and crystalline components

Depending on where the sediment is located in an ecosystem, and sometimes depending on the location within the horizontal horizons of the sediments, one can encounter either oxic or anoxic conditions. Oxic zones are characterized by relatively high oxidation potentials (oxidising conditions) and anoxic zones are characterised by relatively low oxidation potentials (reducing conditions).

The oxic/anoxic status of a sediment is important in determining what sediment components might exist, and therefore what metal-binding capacities the sediments might have.

Some of the components present in sediments are also present in soils. Therefore the literature concerning the chemical behaviour of these components both in soils and in sediments were consulted.

METAL BINDING SEDIMENT COMPONENTS IN OXIC CONDITIONS

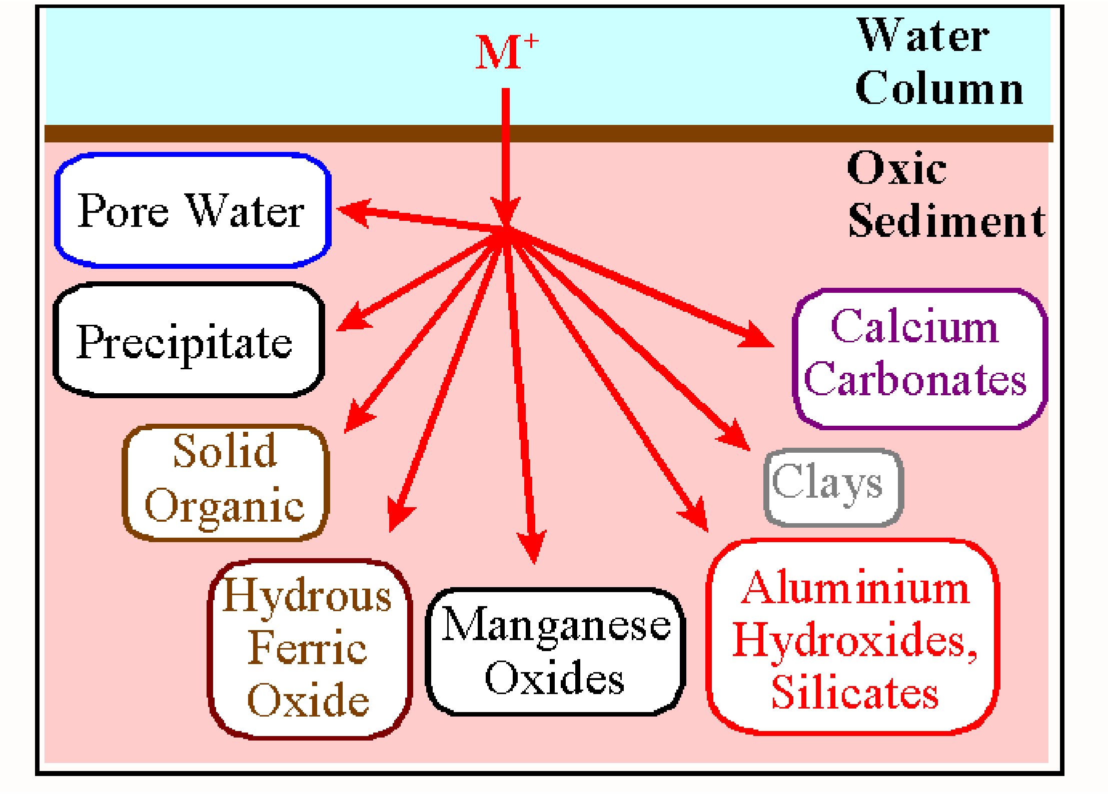

Figure 28: Metal binding phases in oxic sediments

A study of fractionation of metals amongst the components of soils is presented in McBride (1989). The mechanisms of the main reactions have been described by Evans (1989).

Heavy metals have been found to bind to the solid components of oxic soils in the following descending order:

- organic matter (particulate and dissolved humic substances)
- hydrous ferric oxides (amorphous, Goethite)
- manganese oxides (amorphous, Birnessite)
- aluminium hydroxide (amorphous, Gibbsite)
- aluminium silicates (amorphous, allophanes)
- clay minerals
- calcium carbonate (amorphous, calcite)

For some metals, the availability of the metal is dominated by precipitation of a solid, as opposed to sorption to a solid sediment phase. This has been demonstrated for lead in a Dutch sediment by Julius Pretorius (Pers. Comm.).

Sometimes it is difficult to distinguish the mechanisms of adsorption and surface precipitation (Sposito, 1986). Some researchers regard chemisorption and surface precipitation as end members of a sorption continuum (Farley *et al.*, 1985).

Under oxic conditions, and at low levels of metal concentration, precipitation of pure metal compounds is unlikely (Evans, 1989; Brümmer *et al.,* 1986). However, chromium has been observed in soils as precipitated $Cr(OH)_3$ (Rai *et al.,* 1989), and zinc is often found in the form of $ZnCO_3$ at pH greater than 7 (Brümmer *et al.,* 1986).

Much more likely is the mechanism of co-precipitation. The solubility of a metal in a co-precipitate may be orders of magnitude lower than in the pure metal compound.

Organic Matter

Organic matter in sediments is essentially composed of
- humic substances
- biomass of living organisms (plants, animals, microbes)
- detritus, the remains of dead organisms (cellulose, lignin, proteins, lipids etc)
- reactive substances, mainly produced and consumed by microbes (fatty acids, amino acids, sugars, etc)

The most important component of the organic matter is the humic substances, due to the fact that it generally comprises over 90% of the organic matter, and because the other organic fractions are turned over in sediments relatively rapidly, and therefore don't bind metals permanently.

Senesi (1992) defines humic substances as follows:

- humic acid is the non-soluble fraction when $pH < 2$
- fulvic acid is the fraction soluble under all pH conditions
- humin is the non-soluble fraction

The dissolved organic fraction is relatively hydrophobic, and bears a net negative charge. Therefore this fraction adsorbs readily on the other solid sediment components (organic matter, (hydrous) metal oxides, hydroxy silicates and clay).

Sager (1992) found that humic acid adsorbs much more strongly to hydrous ferric oxides than to manganese oxides. Sorption depends on the hydrophobicity of the solid surface, and the pH. Substantial adsorption of humic acid to the metal oxides may change the overall charge on the solids from positive to negative (Gu *et al.*, 1994; Tipping and Cooke, 1982). This charge reversal might have implications on the metal-binding capacities of the solids.

Desorption of humic substances occurs much more slowly than adsorption, implying that the mechanism of sorption of the organic matter to the solids is multi-site binding (Gu *et al.*, 1994). The great differences in these rates imply that for most purposes adsorption of humic acids to (hydrous) metal oxides is an essentially irreversible process. Factors increasing the desorption of organic matter from (hydrous) metal oxides include sudden elevation in pH, and dissolution of the solid phase by reduction (e.g. of Fe^{3+} to Fe^{2+}, and MnO_2 to Mn^{2+}).

While outer-sphere, electrostatic binding occurs (notably at high metal loading), inner sphere, covalent binding of metals to various functional groups of humic substances dominates (Senesi, 1992; Allen and Yin, 1996; Gooddy *et al.*, 1995).

McBride (1986) presents a typical affinity sequence for binding of metals to organic matter as follows:

Cu > Ni > Pb > Co > Ca > Zn > Mn > Mg

Elliott *et al.* (1986) demonstrated that the affinity of organic matter for cadmium is stronger than that for zinc.

Extent of metal loading and the presence of competing metals contribute to extent of adsorption. It is suspected that calcium might occupy a large proportion of binding sites in humic substances.

Extent of adsorption is pH dependent. Organic matter maintains a high sorption capacity for metals even at low pH, while metal oxides lose their cation binding capacity (Brümmer *et al.*, 1986). At low pH organic matter dominates in metal adsorption capacity, whereas metal oxides dominate above pH 5 (Elliott *et al.*, 1986).

(Hydrous) Ferric Oxides

The (hydrous) oxides of iron contribute significantly to the reactive surface area of oxic sediments, due to their presence as small particles and as coatings of other sediment components.

The nature of the iron oxides, and thus their metal-binding potential, varies considerably as a result of the existence of multiple degrees of crystallinity (amorphous to crystalline), multiple configurations in crystal structures, and access to multiple oxidation states.

The thermodynamically most stable forms of iron oxides are the crystalline forms Goethite and Hematite. Goethite is a hydrous oxide. When iron oxides initially form, though, they precipitate from solution as amorphous hydrous oxide, or hydrous ferric oxide (HFO). The overall stoichiometry of the solid is $Fe_2O_3.nH_2O$, where *n* varies from 1 to 3. This compound is highly disordered and porous, with properties more akin to a gel than a solid phase. The surface area is thus very large (probably between 300 and 840 m^2/g (Schwab and Lindsay, 1983)). Hydrous ferric oxide gradually transforms into goethite (Dzombak and Morel, 1990), 2-10% of the Goethite appearing after 15 days.

Adsorption of metals to (hydrous) ferric oxides is pH dependent, and highly specific, with replacement of H^+ on the Fe-O-H entities being the mechanism (Evans, 1989, Forbes *et al.*, 1976). Site densities on amorphous ferric oxide can vary in the range of 0.001-0.01 mol/mol Fe (Dzombak and Morel, 1990).

Hydrous ferric oxide has a high surface area, and a large reactive site density, by comparison to crystalline Goethite.

Inner-sphere (covalent) binding of metals to ferric oxides is the dominant binding reaction, whereas outer-sphere (ionic) binding of metals occurs only at very high metal loading (Brümmer *et al.*, 1986).

The pH dependency of cation binding to hydrous ferric oxides have been explained by various researchers as follows (McBride, 1989; Brümmer *et al.*, 1986; Evans, 1989; Elliott *et al.*, 1986):

- pH dependent surface charge
- pH-proportional hydrolysis of metal ions in solution
- acid-catalyzed dissolution of reactive oxide sites

The maximum sorption occurs at a pH slightly lower than the pK_a of hydrolysis of the specific metal ion involved. Thus, the order of binding strength of metals is rougly consistent with the ability of the metals to hydrolyse (Kinniburgh *et al.*, 1976; Brümmer *et al.*, 1986; Elliott *et al.*, 1986):

$$Hg > Pb > Cu > Zn > Ni > Cd > Co > Sr > Mg$$

Anions also bind to (hydrous) ferric oxides. In some cases they can act as bridging ligands that enhance the binding of metals to (hydrous) ferric oxides. Phosphate and sulphate have been found to enhance sorption of zinc (Schuman, 1986) and sulphate has been found to enhance sorption of cadmium (Benjamin and Leckie, 1982).

Other ternary complexes of the form FeO-M-L have been seen in the case of copper (McBride, 1985). In these cases, the concentration of ligands, L, determine the extent of metal binding to the oxide surface, with higher ligand concentration decreasing sorption of the metal to the oxide surface (Brümmer *et al.*, 1986).

Arsenate binds strongly at low pH, where the ferric oxide surface is positively charged. Chromate (Cr(VI)) exhibits similar behaviour (Masscheleyn *et al.*, 1991).

Hydrous ferric oxide has a positive surface charge below pH 7.9-8.2 (Dzombak and Morel, 1990).

Manganese Oxides

The oxides of manganese are similar to those of iron in that they have a high surface area and are present in forms varying in degree of crystallinity and in crystal structure.

Manganese is usually present in the form of amorphous and crystalline manganates, with an overall stoichiometry of Mn_nO_{2n}. The most frequently encountered manganese mineral is Birnessite, where $n = 7$ (Paterson *et al.*, 1991).

Manganese oxides are usually positively charged, with the pH at which the oxide is neutral varying across the broad range of 8.2 - 2.5.

Manganese oxide binds metals relatively strongly. The mechanism is generally covalent bonding of the metal to surface $Mn\text{-}O^-$ groups.

Manganese binds particularly strongly to Pb^{2+}, Co^{2+}, Cu^{2+} and Ni^{2+} (Golden *et al.*, 1986).

Calcium Carbonates

Calcium carbonate occurs in some sediments under pH conditions above 7.5. Calcite is the dominant form, while substitutions of magnesium for calcium can occur up to 10% (Loeppert *et al.*, 1994). These minerals can be considered a solid solution of dolomite in calcite.

Calcite dissolves on decreasing the pH and on increasing the partial pressure of CO_2 (?). The mineral precipitates with increasing pH, but the precipitation reaction can be significantly kinetically inhibited, resulting in supersaturations of up to 40 (Sager, 1992).

While the cation sorption capacity of calcite is relatively weak, organic substances can adsorb strongly to calcite, thereby substantially changing the metal-binding capacity of the mineral.

Adsorption of metal onto calcium carbonate minerals is very weak by comparison to the other components of sediments. However, at high pH, calcite has been known to bind to certain cations, cadmium in particular. This effect seems to depend on the size of the metal ion (Davis *et al.,* 1990).

METAL BINDING SEDIMENT COMPONENTS IN ANOXIC CONDITIONS

Reactive components present in the solid phase under reducing conditions are mainly the following (Ankley *et al.*, 1994; Zhuang *et al.*, 1994; Paterson *et al.*, 1991).

- organic matter
- ferrous sulphides (amorphous, mackinawite, greigite)
- manganese sulphide (solid solution in FeS)
- other transition-metal sulphides (solid solution in FeS)
- ferro and manganese carbonate

Under intermittent reducing conditions the following may also be present:

- ferrous carbonate
- manganese carbonate
- hydrous ferric oxides (e.g. lepidocrite)
- manganese oxides

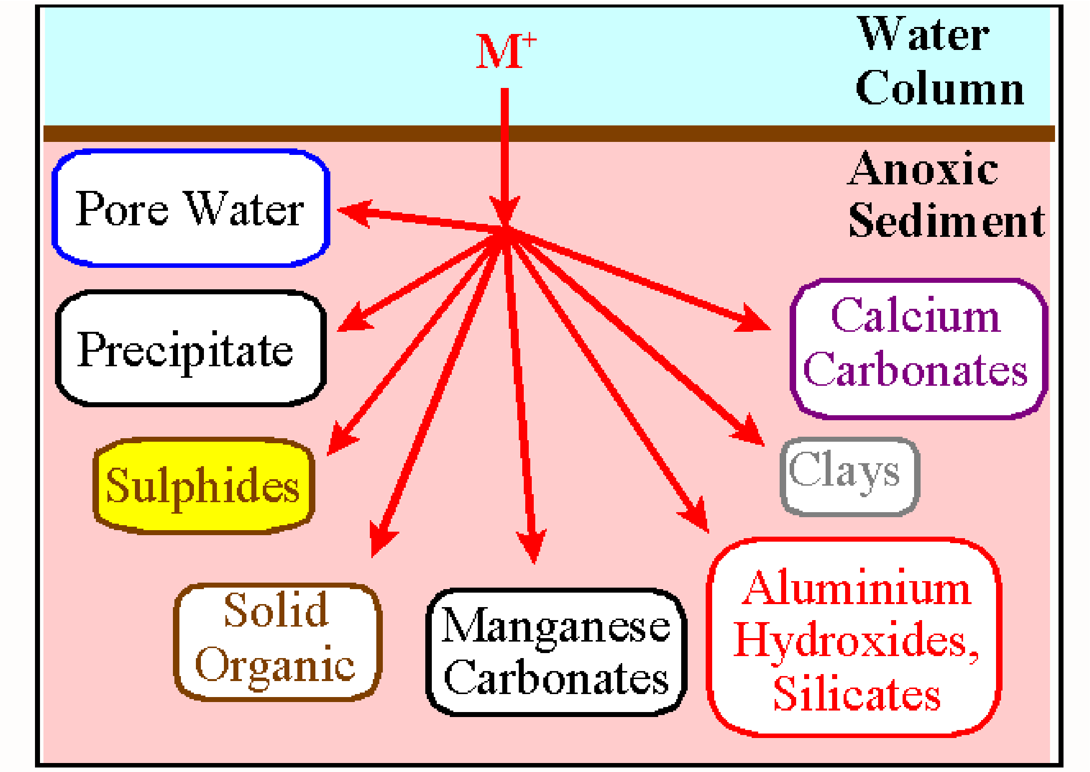

Figure 29: Metal binding components of anoxic sediments

Under anoxic conditions, (hydrous) iron oxides are either absent, or present in very small amounts.

In contrast, iron sulphide may be present in high concentrations.

All transition metals, with the exception of chromium, are expected to be present as sulphides.

Heavy metals have been found to bind to the components of anoxic sediments in the following descending order:

- sulphide
- organic matter (particulate and dissolved humic substances) (especially Cu binding)

The following components may be present, but binding to them is negligible by comparison to that of the iron sulphide and organic matter.

- hydrous metal oxides
- aluminium silicates
- clay minerals
- calcium carbonate

As above, there is an equilibrium between metals on the solid components, and those in the pore waters.

Sulphide Component

The rate of formation of ferrous sulphides substances seem to be dependent on reductive complexation of Fe(III) at the mineral surface by sulphides and organic substances like fulvic acids, oxalic acid and acetic acid. The process may also be mediated by microbial enzymatic reactions (Stumm and Schultzburger, 1992).

Therefore, the presence of decomposing organic matter is very important in the formation of ferrous sulphides.

Pyrite (FeS_2) has been found in ageing sediments. It forms when ferrous sulphide reacts with an excess of sulphide. It has a very low solubility (Tipping *et al.*, 1984).

Current evidence indicates that the formation of the sulphide phase depends on the presence in the system of reactive organic carbon. One possible route of formation is the reduction of sulphate by microbes (e.g. Sulphate Reducing Bacteria), using carbon as a reducing agent, with the concomitant production of carbonate.

Due to the highly insoluble nature of metal sulphides, precipitation of metal sulphide minerals are not dependent on metal concentration *per se*, but due to the ratio of metal to sulphide.

Rates of formation of metal sulphides are extremely high, so that the formation of these components can be said to be instantaneous by comparison with most other geochemical processes.

The order of increasing stability of metal sulphides is (Ankley *et al.*, 1994, Zhuang *et al.*, 1994):

$$Cu > Pb > Cd > Zn > Ni$$

and

$$Cd > Zn > Fe$$

Chemical speciation calculations by JESS suggest the following order of stability:

$$Cu > Pb > Cd > Ni > Zn > Fe$$

The current understanding of binding of metals to the sulphide phase is as follows: Sulphide exists in sediments primarily as the (amorphous) ferrous sulphide. Ferrous sulphide is not as stable as most other metal sulphides, and introduction of any other metal results in *replacement* of iron by the metal in the sulphide phase, resulting in a solid solution of iron and metal sulphides. Iron will then probably manifest in the solution phase.

As iron is depleted by replacement, the more stable metal sulphide phase will dominate until it is the only sulphide phase. Introduction of a new metal which has a sulphide complex of greater stability will result in replacement of the previous one. If the metal that is introduced has less stability as a sulphide, it will bind to the organic component or remain in the solution phase.

Coprecipitation of metals also occurs with iron sulphide in the form of crystalline pyrite (Ankley *et al.*, 1994, Zhuang *et al.*, 1994). Pyrite also adsorbs metals onto its surface and this adsorption is strongly pH dependent, probably relating to the hydrolysis of the metal ion (Sager, 1992).

Organic Matter

Humic substances are relatively inert to decomposition in anoxic condtions, particularly at low pH.

The behaviour of organic matter with respect to metal complexation and binding to other sediment phases is as dealt with above under "Components present in oxic conditions".

If the sulphide phase is not present, due to lack of organic carbon, or it has been entirely converted from the ferrous form to a very much more stable metal sulphide, then it will be unavailable for binding of metals.

Under these conditions, the organic component is the next most likely repository of metals.

The binding of metals to the organic phase occurs very much the same in anoxic sediments as it does in oxic sediments. Differences between metal partitioning in the two scenarios occur when the metal concerned changes its oxidation state in response to the reducing environment of the anoxic sediment.

APPENDIX 2: CONSIDERATIONS WITH RESPECT TO SEDIMENT SAMPLING, HANDLING AND ANALYSIS

The following section is taken from Wade et al., (1998).

SAMPLING WITH CORE SAMPLERS

Sediment coring is generally accomplished by inserting a cylindrical tube into the sediment, closing the top of the tube to create suction, and withdrawing a sediment core. Subsurface sediment corers differ greatly in size and complexity. Small push corers and small gravity corers can be retrieved by hand and used from a small boat (Washington State Department of Ecology, 1995).

Core samplers are limited to less-compacted, fine-grained sediments. Some core samplers also have certain limitation in some situations. Most corers do not work well in sandy sediments and in general collect less sediment than do dredge samplers which may provide inadequate quantities for some toxicity studies. Small corers tend to increase bow (pressure) waves (disturbing the surface sediments) and compaction, thus altering the vertical profile. However these corers provide better confidence limits and spatial information when multiple cores are obtained.

Care must be taken in subsampling from core samples, since surface sediments might be disrupted in even hand-held core collection. Subsampling, compositing, or homogenising of sediment samples is often necessary, and the optimal methods will depend on the study objectives. Important considerations that may influence sediment test results and interpretations include loss of sediment integrity and depth profile; changes in chemical speciation via oxidation and reduction or other chemical interactions; disruption of chemical equilibrium resulting in volatilisation, sorption, or desorption; changes in biological activity; completeness of mixing; and sampling container contamination. In most studies of sediment toxicity, it is advantageous to subsample the inner core area (not contacting the sampler), since this area is most likely to have maintained its integrity and depth profile and not be contaminated by the sampler. subsamples of the depositional layer of concern, for example, the top 1 to 2 cm, should be collected with a nonreactive sampling tool, such as a polytetrafluoroethylene-lined calibration scoop.

Due to the large volume of sediment that is often needed for toxicity or bioaccumulation tests and chemical analysis, it might not be possible to use subsampled cores because of sample size limitations. In those situations the investigator should be aware of the above considerations and their possible affect on test results as they relate it in situ conditions (Burton, 1992).

SAMPLE HANDLING PROCEDURES

Once sediment samples are collected, it is important, in most situations, to maintain an anoxic environment. The majority of fine-grained sediments, which are of concern in toxicity assessments, are anaerobic below the top few surface millimeters, and any introduction of oxygen will likely alter the valence state of many ionic chemicals and result in sediment toxicant(s) bioavailability and toxicity levels that differ from in situ conditions. To protect sediments from oxygenation, the use of a glove box with an inert gas supply for subsampling and processing, e.g., preparation of sediments for centrifugation, may be necessary (Burton, 1993).

Ideally, chemical analysis should be conducted on discrete sediment samples collected from a single cast of the sampling device at each station. In practice, it is often necessary to collect more than one sample per station when the proposed analysis (including chemical analysis, physical analysis, and toxicity testing) require larger volumes of sediment from the targeted depth (e.g., 0-10 cm) than can be acquired in a single cast of the sampling device. In such cases, multiple casts of the sampling device should be made at the same station, taking care to sample as close as possible to other casts at that station.

Sediments collected from the targeted depth with each cast of the sampling device should be combined with the other sediments collected from that depth at that station and, after removal of unrepresentative material (e.g., woody debris, shells, rocks) at the discretion of the scientist, homogenised to a uniform appearance by stirring. Subsamples should then be taken from this composite sediment sample for chemical analysis, physical analysis, and toxicity testing, if required.

IDENTIFICATION OF SEDIMENT CHEMICAL PHASES AND ASSOCIATED METALS

Sequential Extraction Techniques

In a previous study (Wade et. al, 1998), a number of sequential extraction procedures were investigated and compared.

The sequential extraction procedure chosen for the current study is one detailed by Ure et al. (1993). This extraction procedure has been adopted in Europe as a standard protocol (the BCR protocol - Community Bureau of Reference, Paris, France).

The procedure was validated in South Africa by Coetzee et al. (1995), using model sediments, and was subsequently used in studies for determination of solid-phase speciation of metal ions (Gouws and Coetzee, 1997; Wade et al., 2000).

The sequential extraction procedure discriminates the total content of the metal over various operationally defined fractions in the solid phase. This solid phase “Speciation" is obtained by employing sequential extraction procedures. Numerous schemes were found in the literature, most purporting to discriminate between the following:

1) exchangeable metals plus metals associated with calcium carbonate;
2) metals present in easily reduced phases, mainly metals associated with manganese oxides and partly also associated with amorphous iron oxides;
3) metals associated with amorphous and poorly crystalline iron oxides;
4) metals associated with organic matter or present as metal sulphides; and
5) a residual fraction.

A detailed literature review on SE procedures is given by Tessier and Campbell (1988).

Sequential extraction (SE) with different extraction agents by definition leads to different metal fractions. Whether the fractions obtained do indeed represent the various pools is questionable. SE in itself does not lead to the possibility of predicting the interaction of a metal with the solid phase. However, in the current study, it is not critical to determine which phase is binding which radionuclides, since all that is required is knowledge of what emanates from the Mooi River sediments under which chemical conditions.

CHARACTERISTICS OF SEQUENTIALLY EXTRACTED SEDIMENT FRACTIONS

A short description of the five fractions most likely to be relevant in assessing the effect of changing environmental conditions on polluted sediments is given below. A more detailed discussion may be found in the literature (Tessier et al., 1979).

Fraction 1: Exchangeable

Metals extracted from the readily exchangeable fraction would include weakly adsorbed metals, particularly those retained on the sediment surface by relatively weak electrostatic interaction, and those that can be released by ion-exchange processes. Changes in the ionic composition of the water would strongly influence the adsorption-desorption and ion-exchange processes of metal ions with the major constituents of sediments like clays, and the hydrated oxides of iron and manganese. The Mooi River is the recipient of the effluents of mining, industrial and domestic activities, and can be expected to experience fluctuations in ionic character.

Fraction 2: Bound to carbonates

Significant amounts of trace metals can be coprecipitated with carbonates (e.g. calcite), which may be present in sediments of the Mooi River catchment, owing to the predominance of dolomites in the region.. Lowering of the pH of the river could cause remobilisation of metals from this fraction. The region is prone to acid rain, and could experience accidental release of acid from mining activities.

Fraction 3: Bound to iron and manganese oxides

Iron and manganese oxides have large surface areas for adsorbing trace metals. These oxides can be present in sediments as concretions, cement between particles, or as coatings on particles. Reduction of Fe(III) and Mn(IV) under anoxic conditions would cause dissolution, and could release absorbed trace metals.

Fraction 4: Bound to organic matter and sulphides

Particulate organic matter binds some metals relatively strongly. The organic matter, which largely consists of microbially degraded plants and other organisms, has a multiplicity of adsorption sites of varying strengths. If the Mooi River were to run dry, the sediments would be exposed to oxygen, with concomitant potential release of stored metals.

Sulphides are also extracted in this oxidation step. Many metals form highly insoluble sulphide compounds, and many more can be co-precipitated with sulphides. Most sulphide in natural sediments is in the form of iron sulphides.

Fraction 5: Residual or inert fraction

The residual fraction largely consists of mineral components where metals are firmly bonded within the crystal structure of the minerals comprising the sediment. These metals are not likely to be released into solution under normal environmental conditions, and were not investigated in this study.

APPENDIX 3: GENERAL CONSIDERATIONS OF ESTIMATING RISK

The following section has been modified from Wade (2000).

The current study is a Tier 1 investigation of risk due to exposure to radionuclides. In Tier 1 risk assessments, very simple exposure data, such as environmental concentrations, are compared to benchmarks, such as legislative limits.

Formal radiological risk assessments typically involve estimates of dose, in terms of scenarios and pathways, and typically involve Tier 2 or higher methodologies.

The following section introduces the concept of risk in terms of conventional chemical exposures.

GENERAL CHARACTERISTICS OF RISK ASSESSMENTS

The purpose of a risk assessment is generally to estimate the likelihood of adverse effects of a process (stressor) on a sector of a population (receptor).

Exposure and Effects Estimation

There are two components of such a risk assessment: Exposure Estimation and Effect Estimation.

In radiological risk assessments, exposure is usually thought of as the potential dose received by the receptor. Effects of the dose are those observed in trials and tabulated in legislation.

Probabilistic profiles and the Quotient method

The probabilistic risk assessment is the most sophisticated risk assessment in current use. In a probabilistic risk assessment, probability profiles of dose are generated in scenarios, and overlayed on probabilistic effects profiles. The intersection of the profiles is proportional to the risk.

The most widely used risk assessment procedure is the "quotient method". This method uses a "worst case" single estimate for exposure, an estimate of effect based on the most sensitive section of the population, and overlays them in a quotient as follows:

$$Risk = \frac{Highest\ dose}{Most\ sensitive\ effect}$$

In many cases, the "effect" is taken as some numerical limit emanating from legislation.

In the current study, the dose is estimated as a surrogate by the measured concentration of U-238 per kilogram of sediment, and the effect is taken as the IAEA limit for unconditional closure of a facility.

Tiers of Risk Assessments

The purpose of the exposure assessment should be very clear. Exposure assessments can be used in risk assessments, or for determination of status and trends, or for epidemiological studies [1,2].

Knowledge of the scope of the assessment is critical. 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 [1].

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 [1].

Risk assessments usually follow a tiered approach, in which the scope if the assessment is narrowed upon successive iterations [4].

The first tier of the risk assessment, termed Tier I, uses the most conservative assumptions, and utilises "worst case" scenarios.

Subsequent tiers of the risk assessments address the exposure and effects determinations in greater and greater detail.

If an acceptable level of risk is established in any tier, the iterative process is stopped, and there are no subsequent tiers.

THE ROLE OF EXPOSURE SCENARIOS IN EXPOSURE ASSESSMENT

Exposure scenarios are tools to help the risk assessor develop estimates of exposure, dose and risk. Estimates derived from scenarios can be used to develop a series of exposure and risk descriptors. Exposure scenarios can often assist risk managers in estimating possible impact of certain mitigation or control options [1]. Scenarios may have a limited ability to accurately characterise exposures, and scenarios may be developed with policies in mind that are not readily apparent to the risk manager. There is a need for very clear communication on the dynamics underlying the scenarios [4].

Scenarios can be used to quantify exposure and dose; as input of estimates into risk descriptors, and as a tool for option evaluation.

GENERAL PROCEDURE FOR EXPOSURE ANALYSIS

Describing dimensions of exposure

The first practical step in developing the exposure is the description of the dimensions of exposure, i.e. the Intensity, the temporal extent (duration, frequency and timing and sequence of exposure events), and the spatial extent.

Evaluating Exposure Pathways

In this step, the following actions are performed:

- Describe pathways
- Verify Pathways
- Rank Pathways by contribution to total exposure.

Identifying Receptor

The receptor of the stressor should be identified, in order to assist in estimating exposure.

Estimating exposure and dose

Exposure assessments can be from the perspective that begins with a biological receptor, or it can be from the complimentary perspective of the contaminant emission into the environment, or observation that contamination exists at certain sites [4].

In the latter Emission-based exposure calculations, exposure is estimated using concepts of contaminant fate and transport, or by use of monitoring data for retrospective risk assessments. Models are usually used, based on monitoring data [4].

APPENDIX 4: MASSES USED IN SEDIMENT SEQUENTIAL CHEMICAL EXTRACTION

Sample name	Weight used (g)
TUD 1	10.0084
ATT 2 rep	8.3959
DON 3	10.0313
ABE 4	10.0092
HAR 5	9.988
SLU 6	10.0019
A-C 7	10.0068
BOS 8	10.0584
KKD 9	10.0019
MUIS 10	10.0642

APPENDIX 5: SEDIMENT RADIONUCLIDE SAMPLING DATA SHEET

Site code:

Date:_________________ Time :_________________

GPS Readings:

Latitude :_________________ Longitude :_________________

Altitude :_________________

Water Chemistry

pH :_________________ Temp (°C):_________________

EC (μS/cm):_________________ DO (mg/ℓ):_________________

Redox (mV):_________________

SASS4 Score:_________________

Gamma Spectra Filename :_________________

APPENDIX6: DATA USED IN CHEMICAL MODELLING

DWAF Water Sampling Station Identifiers

Site Name	Latitude_DMS	Longitude_DMS	Latitude_DD	Longitude_DD	First sampling date	Last sampling date	Sample Type	Number of samples
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	260952	274602	-26.1644	27.7672	04/02/97	24/06/97	S21	76
WONDERFONT SPRUIT RAIL BRIDGE (BETW TURK SHAFT AND FIRST WEST GOLD MINE)	260803	274600	-26.1342	27.7667	04/02/97	24/06/97	S21	74
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	261557	274158	-26.2658	27.6994	04/02/97	17/12/97	S21	96
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	260952	274602	-26.1644	27.7672	04/02/97	24/06/97	S21	76
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	261557	274158	-26.2658	27.6994	04/02/97	17/12/97	S21	96
WONDERFONTEIN EYE AT WONDERFONTEIN-(CANAL)	261847	272920	-26.3131	27.4889	29/12/78	04/03/98	S20	422
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	261557	274158	-26.2658	27.6994	04/02/97	17/12/97	S21	96
WONDERFONTEIN SPRUIT AT EXIT OF 1M PIPELINE VENTERSPOST GOLDMINE	261935	272438	-26.3264	27.4106	16/04/80	04/03/98	S25	241
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	261718	274009	-26.2883	27.6692	10/01/80	04/03/98	S21	341
WONDERFONTEIN SPRUIT AT GEMSBOKFONT. D/ST DONALDS.DAM	261703	274049	-26.2842	27.6803	09/01/80	07/01/98	S21	160
WONDERFONTEIN SPRUIT AT LAW WATER BRIDGE TO ABE BAILEY NATURE RESURVE	261925	272115	-26.3236	27.3542	05/02/97	17/12/97	S21	95
WONDERFONTEIN SPRUIT AT LUIPAARDSVLEI	261326	274424	-26.2239	27.7400	09/05/79	21/05/97	S21	797
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	261718	274009	-26.2883	27.6692	10/01/80	04/03/98	S21	341
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	262605	270907	-26.4347	27.1519	04/02/97	24/06/97	S21	74
WONDERFONTEINSPRUIT AT DAM OVERFLOW HARRY'S DAM (UITSPANNING - WONDERFON	262010	272015	-26.3361	27.3375	04/02/97	17/12/97	S22	52
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	262605	270907	-26.4347	27.1519	04/02/97	24/06/97	S21	74

Mean Concentrations of Water Quality Variables[1]

Site Name	Site Number	STATISTIC	PH	EC	TDS	CA	MG	K	NA	TAL	CL	F	SI	SO4	NH4	NO2_NO3	KN	PO4	TP
MOOIRIVIERLOOP AT BLAAUWBANK WELVERDIEND (RAIL BRIDGE)	C2H075Q01	MEAN	7.2	124.6	923.6	108.3	42.5	10.6	102.2	78.6	84.3	0.4	5.5	440.7	0.5	6.2	46.4	0.8	7.2
MOOIRIVIERLOOP (RIVER) AT WONDERFONTEIN	C2H032Q01	MEAN	7.3	93.2	682.9	92.6	37.3	5.2	54.6	103.3	30.7	0.4	6.5	323.4	0.1	3.7	0.2	0.1	0.1
MOOIRIVIERLOOP (RIVER) AT BLAAUWBANK	C2H069Q01	MEAN	7.4	146.8	1055.3	124.6	46.7	11.3	124.9	64.8	112.4	0.4	6.4	522.2	1.0	7.1	2.4	0.4	1.1
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	C2H153Q01	MEAN	7.4	121.4	973.2	212.7	25.0	4.5	24.0	81.3	16.1	0.2	5.0	580.0	2.7	1.8	0.0	0.1	0.0
WONDERFONT SPRUIT RAIL BRIDGE (BETW TURK SHAFT AND FIRST WEST GOLD MINE)	C2H152Q01	MEAN	4.4	175.9	1408.4	210.0	84.0	9.3	42.1	25.0	27.7	0.1	9.6	989.8	9.3	0.7	0.0	0.0	0.0
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MEAN	8.0	92.9	697.5	103.8	24.4	7.8	61.9	153.3	39.7	0.3	3.9	269.1	0.1	0.8	0.0	0.0	0.0
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	C2H153Q01	MEAN	7.4	121.4	973.2	212.7	25.0	4.5	24.0	81.3	16.1	0.2	5.0	580.0	2.7	1.8	0.0	0.1	0.0
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MEAN	8.0	92.9	697.5	103.8	24.4	7.8	61.9	153.3	39.7	0.3	3.9	269.1	0.1	0.8	0.0	0.0	0.0
WONDERFONTEIN EYE AT WONDERFONTEIN-(CANAL)	C2H030Q01	MEAN	7.7	76.9	560.4	62.6	37.3	3.1	44.8	117.1	28.9	0.3	7.0	225.8	0.1	3.5	0.3	0.0	0.0
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MEAN	8.0	92.9	697.5	103.8	24.4	7.8	61.9	153.3	39.7	0.3	3.9	269.1	0.1	0.8	0.0	0.0	0.0
WONDERFONTEIN SPRUIT AT EXIT OF 1M PIPELINE VENTERSPOST GOLDMINE	C2H080Q01	MEAN	7.6	94.0	699.5	92.4	33.6	6.2	64.6	104.2	34.8	0.4	5.6	333.4	0.1	3.0	0.0	0.1	0.0
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	C2H025Q01	MEAN	7.7	129.5	1019.7	174.2	33.2	10.4	77.9	102.3	53.6	0.4	2.9	540.8	0.1	1.5	0.9	0.1	0.2
WONDERFONTEIN SPRUIT AT GEMSBOKFONT. D/ST DONALDS.DAM	C2H024Q01	MEAN	7.1	173.6	1381.5	261.8	45.4	10.4	84.7	30.5	53.8	0.3	3.2	873.9	0.1	3.1	0.5	0.1	0.1
WONDERFONTEIN SPRUIT AT LAW WATER BRIDGE TO ABE BAILEY NATURE RESURVE	C2H157Q01	MEAN	8.1	86.5	631.5	78.2	30.5	7.1	59.5	131.1	36.5	0.3	5.1	246.5	0.4	2.5	0.0	0.6	0.0
WONDERFONTEIN SPRUIT AT LUIPAARDSVLEI	C2H023Q01	MEAN	7.7	165.4	1314.7	235.8	36.7	13.3	95.5	113.8	71.4	0.5	3.6	709.5	0.4	2.8	2.5	0.1	0.0
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	C2H025Q01	MEAN	7.7	129.5	1019.7	174.2	33.2	10.4	77.9	102.3	53.6	0.4	2.9	540.8	0.1	1.5	0.9	0.1	0.2
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	C2H161Q01	MEAN	8.1	109.1	824.7	96.2	49.8	3.8	71.9	194.0	57.8	0.1	8.0	306.0	0.0	0.5	0.0	0.0	0.0
WONDERFONTEINSPRUIT AT DAM OVERFLOW HARRY'S DAM (UITSPANNING - WONDERFON	C2H175Q01	MEAN	8.4	91.2	680.9	84.2	36.4	5.8	60.9	134.3	36.2	0.4	5.6	283.4	0.1	2.0	0.0	0.3	0.0
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	C2H161Q01	MEAN	8.1	109.1	824.7	96.2	49.8	3.8	71.9	194.0	57.8	0.1	8.0	306.0	0.0	0.5	0.0	0.0	0.0
All Sites	All Sites	Overall Mean	7.5	117.2	898.2	138.3	37.9	7.5	66.7	111.5	46.9	0.3	5.4	453.1	0.9	2.3	2.9	0.1	0.5
All Sites	All Sites	Overall Standard Deviation	2.8	45.1	348.7	56.8	15.1	3.0	26.7	45.3	19.8	0.1	2.1	189.7	0.9	1.1	4.3	0.1	0.7

[1] Data from "Water Quality on Disk"

Maximum Concentrations of Water Quality Variables[1]

Site Number	Site Number	STATISTIC	PH	EC	TDS	CA	MG	K	NA	TAL	CL	F	SI	SO4	NH4	NO2_NO3	KN	PO4
MOOIRIVIERLOOP AT BLAAUWBANK WELVERDIEND (RAIL BRIDGE)	C2H075Q01	MAXIMUM	8.79	243.2	1626	249.2	78	37.29	218	431	406.7	0.88	11.05	773.6	30.75	28.73	46.41	13.515
MOOIRIVIERLOOP (RIVER) AT WONDERFONTEIN	C2H032Q01	MAXIMUM	8.43	184	1339	190	55.1	45.83	153.5	384.5	173.6	1.51	15.2	682.1	5.17	39.6	0.331	2.816
MOOIRIVIERLOOP (RIVER) AT BLAAUWBANK	C2H069Q01	MAXIMUM	9.29	353.7	2527	344.1	124.6	26.44	427.5	187.8	668.1	3.13	14.2	1383.1	28.63	73.61	52.282	12.7
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	C2H153Q01	MAXIMUM	8.42	179	1514	331.6	47.3	10.71	41.6	155.9	20.4	0.36	7.31	1015.7	10.899	3.528	0	0.497
WONDERFONT SPRUIT RAIL BRIDGE (BETW TURK SHAFT AND FIRST WEST GOLD MINE)	C2H152Q01	MAXIMUM	7.55	267	2254	336.4	157.3	16.6	55.6	56	36.8	0.29	17.65	1644.6	21.969	2.527	0	0.093
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MAXIMUM	8.27	114.5	876	125.4	37.4	10.8	82.5	224.2	52.2	0.4	5.36	353.4	0.133	2.249	0	0.037
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	C2H153Q01	MAXIMUM	8.42	179	1514	331.6	47.3	10.71	41.6	155.9	20.4	0.36	7.31	1015.7	10.899	3.528	0	0.497
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MAXIMUM	8.27	114.5	876	125.4	37.4	10.8	82.5	224.2	52.2	0.4	5.36	353.4	0.133	2.249	0	0.037
WONDERFONTEIN EYE AT WONDERFONTEIN-(CANAL)	C2H030Q01	MAXIMUM	9.24	151	1123	180.4	58.1	11.56	130.4	201.4	108.5	0.93	10.32	599.2	3.21	12.439	0.971	1.053
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MAXIMUM	8.27	114.5	876	125.4	37.4	10.8	82.5	224.2	52.2	0.4	5.36	353.4	0.133	2.249	0	0.037
WONDERFONTEIN SPRUIT AT EXIT OF 1M PIPELINE VENTERSPOST GOLDMINE	C2H080Q01	MAXIMUM	9.25	155.9	1342	223.3	56.5	13.32	107	210.6	68.7	3.88	8.78	784.2	1.77	12.88	0	1.152
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	C2H025Q01	MAXIMUM	9.59	217.7	1888	359.1	67.2	16.14	118.5	208.3	89.5	0.96	7.81	1295.4	4.686	11.34	6.95	1.442
WONDERFONTEIN SPRUIT AT GEMSBOKFONT. D/ST DONALDS.DAM	C2H024Q01	MAXIMUM	9.31	298.9	2348	454.6	108.3	28.21	155.5	219.8	95.9	0.69	8.54	1535.8	2.97	17.07	0.797	4.216
WONDERFONTEIN SPRUIT AT LAW WATER BRIDGE TO ABE BAILEY NATURE RESURVE	C2H157Q01	MAXIMUM	8.51	97.4	760	94.2	40.8	9.33	69.6	157	45.7	0.4	6.51	310.1	1.635	3.963	0	0.985
WONDERFONTEIN SPRUIT AT LUIPAARDSVLEI	C2H023Q01	MAXIMUM	12.83	887.8	5243	1276.6	78	44.92	153.8	1885.7	153.5	1.09	13.53	1617.4	8.3	77.16	3.893	0.778
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	C2H025Q01	MAXIMUM	9.59	217.7	1888	359.1	67.2	16.14	118.5	208.3	89.5	0.96	7.81	1295.4	4.686	11.34	6.95	1.442
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	C2H161Q01	MAXIMUM	8.19	114.7	888	106	53.4	7.36	77.1	221.7	61.8	0.16	9.39	360.9	0.12	1.52	0	0.038
WONDERFONTEINSPRUIT AT DAM OVERFLOW HARRY'S DAM (UITSPANNING - WONDERFON	C2H175Q01	MAXIMUM	8.85	97.9	732	98.1	42.3	7.4	68.1	160.2	40.9	0.76	7.76	316.3	0.521	2.696	0	0.434
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	C2H161Q01	MAXIMUM	8.19	114.7	888	106	53.4	7.36	77.1	221.7	61.8	0.16	9.39	360.9	0.12	1.52	0	0.038

[1] Data from “Water Quality on Disk”

Minimum Concentrations of Water Quality Variables[1]

Site Name	Site Number	STATISTIC	PH	EC	TDS	CA	MG	K	NA	TAL	CL	F	SI	SO4
MOOIRIVIERLOOP AT BLAAUWBANK WELVERDIEND (RAIL BRIDGE)	C2H075Q01	MINIMUM	5.32	67.1	417	38.9	15.8	2.24	38.1	6.4	11.2	0.18	0.34	61
MOOIRIVIERLOOP (RIVER) AT WONDERFONTEIN	C2H032Q01	MINIMUM	5.41	44.1	338	23	21.7	1.19	11	21	0	0.11	0	15.7
MOOIRIVIERLOOP (RIVER) AT BLAAUWBANK	C2H069Q01	MINIMUM	3.03	28.7	162	21.3	6.6	0.4	13.2	0	9.6	0	0.27	79.7
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	C2H153Q01	MINIMUM	4.92	71.8	493	63.3	9.4	1.53	16.2	16.6	10.5	0.1	3.82	192.6
WONDERFONT SPRUIT RAIL BRIDGE (BETW TURK SHAFT AND FIRST WEST GOLD MINE)	C2H152Q01	MINIMUM	3.19	100.4	671	76.2	25.1	6.2	20.3	0	15.2	0	3.88	388.4
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MINIMUM	7.7	71.5	498	75.3	15.2	3	30.8	71.1	20.8	0.16	0.64	170.4
WONDERFONTEIN SPRUIT AT RANFONTEIN AZAADVILLE BRIDGE	C2H153Q01	MINIMUM	4.92	71.8	493	63.3	9.4	1.53	16.2	16.6	10.5	0.1	3.82	192.6
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MINIMUM	7.7	71.5	498	75.3	15.2	3	30.8	71.1	20.8	0.16	0.64	170.4
WONDERFONTEIN EYE AT WONDERFONTEIN-(CANAL)	C2H030Q01	MINIMUM	6.11	42.5	263	27.3	14.7	0.68	14.3	27	9.8	0.05	0	62.4
WONDERFONTEIN SPRUIT AT BRIDGE ON THE DOORNKOP RANDFONTEIN ROAD	C2H154Q01	MINIMUM	7.7	71.5	498	75.3	15.2	3	30.8	71.1	20.8	0.16	0.64	170.4
WONDERFONTEIN SPRUIT AT EXIT OF 1M PIPELINE VENTERSPOST GOLDMINE	C2H080Q01	MINIMUM	6.2	50.7	356	27.8	13.9	0.76	5.5	6.9	2	0.02	0.02	42.3
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	C2H025Q01	MINIMUM	5.05	24.6	174	20.8	4.2	1.2	7.2	0	10.2	0.08	0	23.2
WONDERFONTEIN SPRUIT AT GEMSBOKFONT. D/ST DONALDS.DAM	C2H024Q01	MINIMUM	3.41	12.1	94	8.9	1.7	2.33	5.6	0	4.8	0	0	6.8
WONDERFONTEIN SPRUIT AT LAW WATER BRIDGE TO ABE BAILEY NATURE RESURVE	C2H157Q01	MINIMUM	7.73	64.6	445	53.6	19.3	5.61	41.9	94.4	5.9	0.23	3.81	170.9
WONDERFONTEIN SPRUIT AT LUIPAARDSVLEI	C2H023Q01	MINIMUM	3.15	2.6	18	1.8	0.1	0.29	0.7	0	1.1	0	0.06	1.2
WONDERFONTEIN SPRUIT NO 7 AT GEMSBOKFONTEIN	C2H025Q01	MINIMUM	5.05	24.6	174	20.8	4.2	1.2	7.2	0	10.2	0.08	0	23.2
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	C2H161Q01	MINIMUM	7.98	93.7	719	84.4	44.2	2.37	60.7	159.5	52.1	0.09	6.58	257.1
WONDERFONTEINSPRUIT AT DAM OVERFLOW HARRY'S DAM (UITSPANNING - WONDERFON	C2H175Q01	MINIMUM	8.02	82.3	604	73.1	29.7	4.58	53	113.9	30.6	0.25	4.17	253.1
WONDERFONTEIN SPRUIT ON GRAVEL ROAD BRIDGE TO MUISKRAAL	C2H161Q01	MINIMUM	7.98	93.7	719	84.4	44.2	2.37	60.7	159.5	52.1	0.09	6.58	257.1

[1] Data from “Water Quality on Disk”

APPENDIX 7: FIELD WATER QUALITY AND GPS READINGS

Site	Date	Time	Lat Deg	Lat Min	Long Deg	Long Min	Alt (m)	pH	Temp (C)	EC (uS/cm)	DO (mg/l)	Redox (mV)
TUD1	23/07/99	02:10 PM	26	7.879	27	47.785	1721					
ATT2	23/07/99	01:15 PM	26	12.801	27	44.526	1653	8.6	15.8	763	14.6	176
DON3	23/07/99	11:00 AM	26	16.241	27	41.517	1628	8.3	11.5	955	14.5	170
ABE4	22/07/99	02:00 PM	26	19.495	27	21.151	1498	8.6	20.4	828	12	138
HAR5	22/07/99	11:35 AM	26	19.045	27	23.446	1514	8.6	20.4	828	12	182
SLU6	22/07/99	09:30 AM	26	22.49	27	15.141	1476	8.7	14.5	1708	14	171
A-C7	22/07/99	07:45 AM	26	22.324	27	14.433	1476	8.4	6.6	626	8	108
BOS8	21/07/99	01:00 PM	26	31.39	27	7.28		8.1	13.1	749	18	193
KKD9	21/07/99	11:00 AM	26	13.51	27	9.1		8.2	11.7	470	15.1	228
MUIS10	22/07/99	04:00 PM	26	26.183	27	9.086	1439	8.2	11.2	1044	11.5	190

APPENDIX 8: RADIOMETRIC ANALYSES AS RECEIVED FROM THE AEC

Sample				U-238				U-234				U-235				Th-232				Ra-226				Ra-224		
			(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA
2747	x	001	6405	±	480	175	6385	±	319	3213	298	±	45	44	44	±	44	53	2140	±	170	37	166	±	83	112
2747	x	002	954944	±	47747	141	000502	±	50025	2586	44233	±	2212	35	135	±	20	43	7887	±	269	92	195	±	74	76
2747	x	003	780568	±	39028	80	804234	±	40212	1458	36212	±	1811	20	7648	±	382	24	8718	±	230	39	4793	±	299	119
2747	x	004	35571	±	1779	67	35104	±	1755	1226	1650	±	124	17	814	±	61	20	10625	±	183	23	890	±	107	92
2747	x	005	232	±	58	172	3157	±	237	3158	8	±	8	43	7	±	7	52	3801	±	210	85	-45	±	45	335
2747	x	006	10546	±	791	137	10799	±	540	2505	487	±	49	34	5	±	5	41	2667	±	141	20	-58	±	41	272
2747	x	007	7384	±	554	87	7482	±	374	1603	341	±	34	22	11	±	11	26	28980	±	357	12	226	±	63	47
2747	x	008	10526	±	526	70	10845	±	542	1281	488	±	37	17	17	±	17	21	9521	±	175	30	0	±	12	63
2747	x	009	3623	±	272	124	3609	±	271	2277	167	±	25	31	4	±	4	38	243	±	39	59	58	±	29	40
2747	x	010	19437	±	972	115	19343	±	967	2105	899	±	67	29	4	±	4	35	692	±	58	50	37	±	28	91
2747	x	011	16713	±	836	160	17088	±	854	2936	772	±	77	40	19	±	19	48	1839	±	126	23	23	±	23	62
2747	x	012	2926	±	219	64	2937	±	147	1174	134	±	20	16	110	±	17	19	167	±	23	33	65	±	22	20
2747	x	013	41	±	41	133	2445	±	183	2446	6	±	6	33	4	±	4	40	585	±	60	44	47	±	35	116
2747	x	014	3848	±	289	135	3968	±	298	2469	179	±	27	33	4	±	4	41	474	±	56	66	65	±	40	120
2747	x	015	1747	±	131	86	1581	±	119	1581	81	±	12	21	26	±	26	26	2146	±	107	49	50	±	37	122
2747	x	016	1510	±	113	65	1607	±	121	1189	70	±	10	16	108	±	16	20	198	±	30	39	93	±	35	36
2747	x	017	665	±	100	121	2226	±	167	2227	31	±	8	30	4	±	4	37	1715	±	109	51	65	±	38	59
2747	x	018	10901	±	818	131	11108	±	555	2407	506	±	51	33	14	±	14	40	6533	±	231	60	77	±	58	190
2747	x	019	3800	±	285	80	3903	±	195	1462	176	±	26	20	259	±	26	24	4616	±	149	44	90	±	37	41
2747	x	020	4848	±	364	68	4920	±	246	1242	225	±	23	17	76	±	11	20	2773	±	118	53	157	±	50	42
2747	x	021	400	±	60	145	2656	±	199	2657	19	±	19	36	5	±	5	44	3349	±	178	87	0	±	0	80
2747	x	022	84700	±	4235	155	88611	±	4431	2841	3965	±	198	39	5	±	5	47	8200	±	258	75	127	±	57	69
2747	x	023	35352	±	1768	98	36946	±	1847	1796	1637	±	123	24	3	±	3	30	9791	±	252	44	28	±	41	164
2747	x	024	20006	±	1000	70	20330	±	1017	1279	928	±	70	17	2	±	2	21	2115	±	111	39	-18	±	20	147
2747	x	025	213	±	43	136	2495	±	187	2495	10	±	10	34	4	±	4	41	9575	±	311	27	-63	±	49	319
2747	x	026	281096	±	14055	136	283835	±	14192	2502	13104	±	655	34	4	±	4	41	19152	±	423	25	0	±	0	95

		Sample		U-238				U-234				U-235				Th-232				Ra-226				Ra-224		
			(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA
2747	x	027	126732	±	6337	112	126982	±	6349	2049	5860	±	293	28	24	±	24	34	89005	±	794	60	401	±	108	179
2747	x	028	110711	±	5536	62	109839	±	5492	1133	5118	±	256	15	37	±	7	19	15287	±	269	46	530	±	97	48
2747	x	029	143	±	36	128	2351	±	176	2352	6	±	6	32	4	±	4	39	-5	±	21	97	-31	±	34	251
2747	x	030	496	±	74	146	2668	±	200	2669	23	±	23	36	5	±	5	44	96	±	29	24	27	±	27	74
2747	x	031	334	±	50	112	2046	±	153	2047	15	±	15	28	4	±	4	34	81	±	40	115	33	±	33	90
2747	x	032	102	±	20	61	1115	±	84	1115	5	±	5	15	35	±	7	18	26	±	11	25	94	±	36	78
2747	x	033	40	±	40	132	2419	±	181	2420	6	±	6	33	4	±	4	40	34	±	23	73	-19	±	22	160
2747	x	034	23	±	23	134	2458	±	184	2459	6	±	6	33	4	±	4	41	77	±	27	62	-19	±	21	157
2747	x	035	75	±	75	112	2044	±	153	2044	5	±	5	28	4	±	4	34	226	±	42	58	0	±	0	60
2747	x	036	93	±	23	70	1285	±	96	1285	3	±	3	17	4176	±	209	21	43	±	15	31	15	±	15	40
2747	x	037	1	±	1	140	2568	±	193	2568	7	±	7	35	5	±	5	42	126	±	35	60	5	±	38	189
2747	x	038	1988	±	199	146	2680	±	201	2680	92	±	14	36	5	±	5	44	381	±	57	67	0	±	0	69
2747	x	039	1085	±	163	150	2756	±	207	2756	51	±	13	37	5	±	5	45	361	±	49	60	39	±	28	53
2747	x	040	275	±	41	61	1112	±	83	1112	13	±	13	15	52	±	8	18	1	±	5	20	52	±	20	20

Sample			Pb-210 at sampling time				Po-210 at sampling time			
			(mBq/L)		Err.	MDA	(mBq/L)		Err.	MDA
2747	x	001	98	±	397	1654	22	±	78	437
2747	x	002	1470	±	440	871	1199	±	294	187
2747	x	003	65496	±	4370	316	21111	±	2372	67
2747	x	004	3073	±	544	676	1861	±	265	84
2747	x	005	966	±	401	436	192	±	108	277
2747	x	006	874	±	366	829	754	±	187	301
2747	x	007	18091	±	1769	508	6966	±	794	138
2747	x	008	6000	±	788	557	2696	±	381	82
2747	x	009	122	±	268	1061	22	±	38	201
2747	x	010	1066	±	723	2283	-25	±	52	192
2747	x	011	1101	±	663	1914	2588	±	356	366
2747	x	012	2113	±	480	799	69	±	74	166
2747	x	013	629	±	369	568	45	±	63	146
2747	x	014	1325	±	527	1163	-15	±	70	285
2747	x	015	366	±	219	636	901	±	147	208
2747	x	016	1660	±	485	915	-25	±	44	122
2747	x	017	336	±	528	2211	107	±	60	195
2747	x	018	1928	±	642	1546	141	±	93	279
2747	x	019	4193	±	594	172	722	±	125	82
2747	x	020	4135	±	553	146	642	±	167	62
2747	x	021	11	±	196	1023	31	±	57	302
2747	x	022	3890	±	902	1435	83	±	101	219
2747	x	023	7231	±	930	576	2343	±	305	179
2747	x	024	3616	±	540	589	851	±	149	72
2747	x	025	721	±	299	326	201	±	88	96
2747	x	026	9344	±	1404	402	1605	±	268	75
2747	x	027	96460	±	6670	859	22825	±	2498	238
2747	x	028	25277	±	2149	470	2484	±	539	195
2747	x	029	329	±	245	802	-23	±	17	186
2747	x	030	765	±	396	1169	265	±	90	141
2747	x	031	2327	±	444	203	1075	±	156	112
2747	x	032	95	±	163	691	14	±	24	106
2747	x	033	274	±	274	1003	-1	±	54	276
2747	x	034	586	±	297	397	4	±	41	142
2747	x	035	3175	±	610	838	2255	±	268	102
2747	x	036	331	±	191	572	285	±	87	200
2747	x	037	1290	±	407	758	37	±	63	189
2747	x	038	926	±	419	1160	334	±	109	150
2747	x	039	3067	±	711	396	895	±	214	243
2747	x	040	195	±	117	340	27	±	26	99

APPENDIX 9: FIELD GAMMA MEASUREMENTS

Site	Context	K_2O(%)	U (ppm)	Th (ppm)	Rate
TUD1	SUBSTRATE	2.33	721.95	49.13	5110.66
	ORGANICS	0.75	151.36	40.27	1612.57
ATT2	SAMPLE	0.23	20.24	7.64	152.76
	BKG	0.67	9.31	7.47	106.26
DON3	SAMPLE	0.32	6.7	6.3	100.30
	BKG	0.41	9.05	10.94	125.34
ABE4	SAMPLE	0.66	12.18	12.99	165.95
	BKG	0.33	6.36	7.93	106.76
HAR5	SAMPLE	0.7	97.68	10.1	572.48
	BKG	0.19	3.55	4.64	63.23
SLU6	BKG	0.32	7.64	6.94	99.69
	SAMPLE	0.48	93.93	9.78	632.09
	SAMPLE	0.1	83.61	7.98	546.06
	SAMPLE	0.1	77	6.02	440.84
	BKG	-0.08	23.5	4.11	107.02
A-C7	BKG	0.27	25.56	6.78	270.18
	BKG	0.29	13.36	8.83	119.64
	BKG	-0.13	53.61	6.35	311.55
	SAMPLE	1.65	531.31	26.69	3339.32
	SAMPLE	1.58	532.45	24.67	3369.53
MUIS10	SAMPLE	0.16	5.72	5.05	62.82
	BKG	0.44	11.54	6.42	102.5
BOS8	SAMPLE	0.25	-0.17	5.77	45.56
	BKG	0.37	2.2	8.05	74.56
KKD9	SAMPLE	1.09	3.09	4.01	102.7

APPENDIX 10: CONCENTRATIONS OF RADIONUCLIDES IN Bq/kg AND ppm

Concentrations of selected radionuclides in Bq/kg and in ppm from direct measurement and inference from gamma spectroscopy.

Site	Gamma Rate	U (ppm)	Th (ppm)	U (ppm)	Th (ppm)	Extract	U-238 ppm	U-238 Bq/kg	U-234 Bq/kg	U-235 ppm	U-235 Bq/kg	Th-232 ppm	Th-232 Bq/kg	Ra-226 Bq/kg	Ra-224 Bq/kg	Ra-223 Bq/kg	Pb-210 Bq/kg	Po-210 Bq/kg
		from gamma 2π																
TUD1	5111	721.95	49.13	2556	361	1	3.68	45.62	45.47	0.03	2.13	0.08	0.31	15.24	1.18	-0.57	0.70	0.15
						2	695.76	8627.39	9038.98	5.00	399.62	0.30	1.22	71.25	1.76	6.50	13.28	10.83
						3	899.79	11157.39	11495.68	6.47	517.62	26.92	109.31	124.61	68.51	25.39	936.19	301.76
						4	50.77	629.49	621.22	0.36	29.20	3.55	14.41	188.03	15.76	-1.65	54.37	32.93
						Total	1649.99	20459.89				30.85						
ATT2	153	20.24	7.64	77	10	1	0.15	1.91	26.01	0.00	0.07	0.01	0.06	31.32	-0.37	-2.65	7.96	1.58
						2	9.09	112.74	115.45	0.07	5.20	0.01	0.05	28.51	-0.62	-2.28	9.34	8.06
						3	10.06	124.80	126.45	0.07	5.76	0.05	0.19	489.78	3.82	-0.56	305.75	117.73
						4	17.02	211.01	217.40	0.12	9.79	0.08	0.34	190.85	0.00	-2.36	120.28	54.04
						Total	36.33	450.46				0.16						
DON3	125	6.7	6.3	63	3	1	2.64	32.69	32.57	0.02	1.51	0.01	0.04	2.19	0.53	-0.20	1.10	0.20
						2	16.32	202.43	201.45	0.12	9.36	0.01	0.04	7.21	0.39	-1.39	11.10	-0.26
						3	9.49	117.68	120.32	0.07	5.43	0.03	0.14	12.95	0.16	-0.25	7.75	18.22
						4	4.11	51.02	51.21	0.03	2.34	0.47	1.92	2.91	1.14	-0.54	36.84	1.19
						Total	32.57	403.83				0.52						
ABE4	166	12.18	12.99	83	6	1	0.03	0.36	21.40	0.00	0.06	0.01	0.04	5.12	0.42	-0.15	5.51	0.39
						2	2.75	34.09	35.15	0.02	1.59	0.01	0.04	4.20	0.58	0.03	11.74	-0.13
						3	1.87	23.16	20.95	0.01	1.07	0.08	0.34	28.44	0.66	1.48	4.85	11.94
						4	2.14	26.53	28.22	0.02	1.23	0.47	1.90	3.47	1.63	0.70	29.16	-0.43
						Total	6.78	84.13				0.57						
HAR5	572	97.68	10.1	286	49	1	0.50	6.17	20.67	0.00	0.29	0.01	0.04	15.92	0.61	1.63	3.12	0.99
						2	7.64	94.73	96.53	0.06	4.40	0.03	0.12	56.77	0.67	0.96	16.75	1.23
						3	4.59	56.93	58.48	0.03	2.63	0.96	3.89	69.16	1.35	-1.52	62.82	10.82
						4	6.85	84.99	86.25	0.05	3.95	0.33	1.34	48.62	2.74	7.92	72.49	11.25
							19.58	242.82				1.33						
SLU6	632	93.93	9.78	316	47	1	0.27	3.32	22.02	0.00	0.15	0.01	0.04	27.76	0.00	0.31	0.09	0.26
						2	52.37	649.38	679.37	0.38	30.40	0.01	0.04	62.87	0.98	9.15	29.82	0.64
						3	36.50	452.63	473.05	0.26	20.97	0.01	0.04	125.36	0.36	32.83	92.59	30.00
						4	27.18	337.05	342.52	0.20	15.63	0.01	0.04	35.63	-0.30	26.25	60.93	14.34
						Total	116.32	1442.39				0.04						

Site	Gamma Rate	U (ppm)	Th (ppm)	U (ppm)	Th (ppm)	Extract	U-238 ppm	U-238 Bq/kg	U-234 Bq/kg	U-235 ppm	U-235 Bq/kg	Th-232 ppm	Th-232 Bq/kg	Ra-226 Bq/kg	Ra-224 Bq/kg	Ra-223 Bq/kg	Pb-210 Bq/kg	Po-210 Bq/kg
		from gamma 2π																
A-C7	3370	531.31	26.69	1685	266	1	0.15	1.90	22.31	0.00	0.09	0.01	0.04	85.64	-0.56	-0.14	6.45	1.79
						2	193.41	2398.33	2421.70	1.40	111.80	0.01	0.04	163.41	0.00	1.95	79.72	13.70
						3	105.28	1305.46	1308.04	0.75	60.36	0.06	0.25	916.84	4.13	52.65	993.63	235.12
						4	166.00	2058.36	2042.15	1.19	95.16	0.17	0.68	284.23	9.86	70.50	469.96	46.19
						Total	464.84	5764.05				0.25						
MUIS10	63	5.72	5.05	32	3	1	0.00	0.01	22.74	0.00	0.06	0.01	0.04	1.12	0.05	0.33	11.42	0.33
						2	1.28	15.91	21.45	0.01	0.74	0.01	0.04	3.05	0.00	-0.57	7.41	2.67
						3	0.63	7.87	20.01	0.00	0.37	0.01	0.04	2.62	0.28	-0.18	22.27	6.50
						4	0.41	5.07	20.52	0.00	0.24	0.24	0.96	0.02	0.96	0.34	3.60	0.50
						Total	2.33	28.87				0.26						
BOS8	45	0.1	5.77	23	0	1	0.11	1.32	21.81	0.00	0.06	0.01	0.04	-0.05	-0.29	0.42	3.05	-0.22
						2	0.33	4.06	21.85	0.00	0.19	0.01	0.04	0.78	0.22	0.37	6.26	2.17
						3	0.27	3.32	20.33	0.00	0.15	0.01	0.04	0.81	0.33	-0.09	23.12	10.68
						4	0.15	1.84	20.04	0.00	0.08	0.16	0.63	0.47	1.70	0.01	1.70	0.25
						Total	0.85	10.54				0.18						
KKD9	103	3.09	4.01	52	2	1	0.03	0.35	21.16	0.00	0.06	0.01	0.04	0.30	-0.17	0.04	2.40	-0.00
						2	0.02	0.22	23.12	0.00	0.06	0.01	0.04	0.72	-0.18	0.12	5.51	0.04
						3	0.06	0.80	21.76	0.00	0.06	0.01	0.04	2.40	0.00	-0.27	33.81	24.01
						4	0.14	1.73	23.88	0.00	0.06	19.12	77.61	0.79	0.27	-0.12	6.15	5.31
						Total	0.25	3.09				19.15						

APPENDIX 11: RATIOS OF ACTIVITY OF SELECTED RADIONUCLIDES

Site	Extract Number	U-234/U-238	U-234/Ra-226	U-238/U-235	Th-232/Ra-224	Pb-210/Po-210	Ra-226/Pb-210
TUD1	1	1.00	2.98	21.46	0.26	4.54	21.77
	2	1.05	126.86	21.59	0.69	1.23	5.36
	3	1.03	92.25	21.56	1.60	3.10	0.13
	4	0.99	3.30	21.56	0.91	1.65	3.46
ATT2	1	13.64	0.83	28.15	-0.16	5.04	3.93
	2	1.02	4.05	21.67	-0.08	1.16	3.05
	3	1.01	0.26	21.68	0.05	2.60	1.60
	4	1.03	1.14	21.55	296.62	2.23	1.59
DON3	1	1.00	14.88	21.71	0.07	5.56	2.00
	2	1.00	27.96	21.63	0.10	-43.11	0.65
	3	1.02	9.29	21.66	0.85	0.43	1.67
	4	1.00	17.57	21.76	1.69	30.84	0.08
ABE4	1	60.20	4.18	6.38	0.09	14.13	0.93
	2	1.03	8.38	21.45	0.07	-91.14	0.36
	3	0.90	0.74	21.56	0.52	0.41	5.87
	4	1.06	8.13	21.61	1.16	-67.05	0.12
HAR5	1	3.35	1.30	21.58	0.06	3.15	5.11
	2	1.02	1.70	21.52	0.18	13.65	3.39
	3	1.03	0.85	21.61	2.88	5.81	1.10
	4	1.01	1.77	21.50	0.49	6.45	0.67
SLU6	1	6.64	0.79	21.60	ERR	0.36	302.16
	2	1.05	10.81	21.36	0.04	46.68	2.11
	3	1.05	3.77	21.59	0.11	3.09	1.35
	4	1.02	9.61	21.57	-0.12	4.25	0.58
A-C7	1	11.72	0.26	21.55	-0.07	3.59	13.28
	2	1.01	14.82	21.45	ERR	5.82	2.05
	3	1.00	1.43	21.63	0.06	4.23	0.92
	4	0.99	7.18	21.63	0.07	10.17	0.60

Site	Extract Number	U-234/U-238	U-234/Ra-226	U-238/U-235	Th-232/Ra-224	Pb-210/Po-210	Ra-226/Pb-210
MUIS10	1	1851.06	20.34	0.21	0.88	34.40	0.10
	2	1.35	7.03	21.51	ERR	2.78	0.41
	3	2.54	7.62	21.45	0.12	3.43	0.12
	4	4.05	1279.13	21.46	0.99	7.25	0.00
BOS8	1	60.69	70.43	6.33	-0.22	-14.02	0.13
	2	107.31	32.01	3.58	-0.23	2.88	0.13
	3	27.22	9.05	14.10	ERR	2.16	0.07
	4	13.81	30.14	27.79	284.98	6.75	0.13
KKD9	1	16.49	-481.12	23.28	-0.13	-530.52	-0.01
	2	5.38	27.90	21.62	0.17	131.76	0.13
	3	6.12	25.18	21.57	0.11	1.41	0.03
	4	10.92	42.29	21.65	0.37	1.16	0.28

APPENDIX 12: TYPICAL GAMMA SPECTRUM