Gold tailings as a source of waterborne uranium contamination of streams - The Koekemoerspruit[#] (Klerksdorp goldfield, South Africa) as a case study

Part I of III: Uranium migration along the aqueous pathway

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Abstract

Tailings deposits from gold and uranium (U) mining in the Witwatersrand basin often contain elevated levels of radioactive and chemo-toxic heavy metals. Through seepage, dissolved U and other metals migrate from tailings deposits via groundwater into adjacent fluvial systems. The subsequent transport through flowing surface water is one of the most effective pathways of distributing contaminants throughout the biosphere. Mechanisms of diffuse stream contamination, as well as the aqueous transportation of U were investigated.

In this paper, geochemical data of water and sediment samples from the Koekemoerspruit (a typical example of a stream affected by gold and U mining in South Africa) are analysed with regards to possible transport and immobilisation mechanisms of U migrating in solution. Ratios between dissolved and solid phases of U for various water-sediment-systems along the aqueous pathway indicated, unexpectedly, significantly lower mobility of U in flowing surface water than in the groundwater system of the floodplain. Correlation of various geochemical parameters suggests co-precipitation of U along with calcium carbonate and iron/manganese-compounds as the main reason for the higher immobilisation rate in the flowing water systems. Owing to redox-initiated precipitation at the interface of reducing groundwater and oxygenated stream water within the bottom sediments, the latter act as a sink and geochemical barrier for U from groundwater sources. The low retention of U in the highly sorptive floodplain sediments on the other hand is explained by the formation of neutral uranyl-sulphate-complexes, which prevent the positively charged U ion from adsorbing onto negative surfaces of clay minerals and organic substances in the floodplain. Evidence for such complexes are sulphate crusts with extremely high U concentrations, which form on topsoil due to capillary fringe effects in dry periods. Due to their high solubility, these crusts are easily dissolved by rain, resulting in concentration peaks of dissolved U in surface runoff.

Keywords: U mobility, immobilisation mechanisms, aqueous pathways, tailings, seepage, sediment-water systems, streams

Introduction

Uranium (U) is a radioactive heavy metal, with average natural background concentrations ranging from <2 to 4 mg/kg (ppm) (Turekian and Wedepohl 1961). However, in the auriferous sediments of the Witwatersrand, U is accumulated up to 1 000 mg/kg (0.1 %). Compared to ore with U grades of 0.3 - 6 % (3 000 - > 60 000 mg/kg) mined in Canada and Australia, this is regarded as low-grade ore (McLean, 1994; Cole, 1998). Therefore, in South Africa U was mainly produced as a by-product of gold, which subsidised the mining costs. Between 1952 (when the first regular U recovery plant was commissioned) and 1991, a total of approximately 170 000 t of U_3O_8 was produced and sold (Ford, 1993; Wymer 2001). After a peak in production in 1980 (some 7 200 t) (Venter, 2001), the U price on the world market - and subsequently U production in South Africa - steadily declined (Cole, 1998; Wendel, 1998). From 26 mines, which at one stage were feeding 18 U recovery plants, only three mines and four plants were left by 1995, producing about 1 500 t U_3O_8 per year (Cole, 1998). Currently, less than 1 000 t/a is produced by South African mines (Venter, 2001).

Owing to the much lower gold content in the ore compared to U (Au-U ratio ranges from about 1:10 to 1:100), relatively large amounts of U are brought to the surface by gold mining operations. After milling and leaching, the remaining ore-material (tailings) is deposited as a solid-water-mixture (slurry) on so-called ‘slimes dams’. Since leaching with sulphuric acid (as most commonly used technology in South Africa) extracted some 90% of the original U content from the ore (Ford, 1993; Wendel, 1998), a tenfold increase of U concentrations is to be expected in tailings which are no longer leached for the radioactive metal. With U production being largely confined to gold mines with above-average grades of U the cessation of U production results in particular high U levels in tailings of such mines. Currently about 6 000 t of U is annually disposed onto slimes dams by gold mining activities in South Africa (Winde and De Villiers, 2002a;b; Winde 2003).

In addition to this most gold tailings produced before 1952 were never leached for U (a few old slimes dams, however, were later reworked to recover U), and therefore also contain U in elevated concentrations as found in the mined ore. Since 1886, when gold mining commenced in the Witwatersrand, about six billion tons of tailings have been produced (Janisch, 1986; Robb and Robb, 1998a;b; Wymer, 2001). With an average U concentra-

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[#] The Afrikaans word “spruit” can be translated as a creek or small stream.

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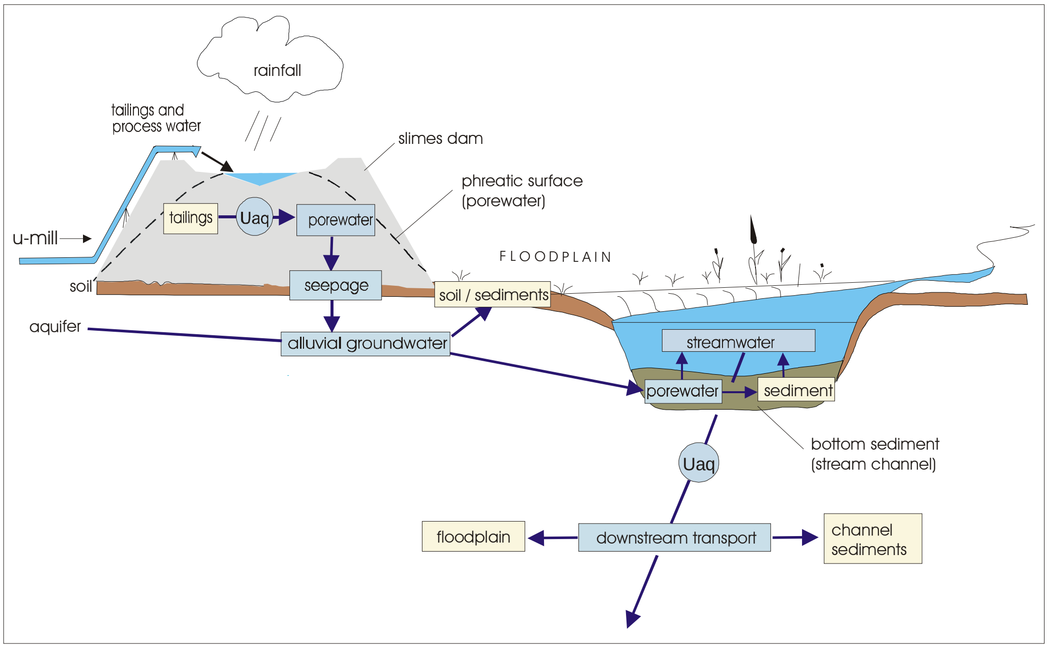

Figure 1
Sediment - water systems of the aqueous pathway along which U migrates from slimes dams into streams (schematic)

tion of 100 mg/kg, slimes dams of gold mines in the Witwatersrand contain higher U concentrations than tailings of many genuine U mines, currently exposing about 600 000t U_3O_8 to the biosphere (Winde and de Villiers, 2002a). With a surface area of some 400 km^2 in the Witwatersrand basin alone this constitutes an environmental problem of extraordinary spatial dimensions (Robb and Robb, 1998a).

The contamination of streams by adjacent slimes dams poses a particular risk for the health of people in informal settlements where polluted stream water is often consumed without appropriate treatment. In addition to this, long-term effects on cattle and crop farming and established drinking water supply schemes are also of concern as shown by a number of recently launched projects (Hearne and Bush, 1996; IWQS, 1999; Wade et al., 2000).

The majority of studies into mining-related stream pollution conducted so far focus either on point-discharges of mining effluents or on erosion of tailing particles from slimes dams as main sources of stream contamination. Based on the assumption that the negative annual water balances in most gold mining areas largely prevent the generation of seepage (Funke, 1990), the transport of dissolved U from tailings deposits was long neglected. This assumption, however, is contradicted by a number of more recent studies which suggest that seepage, containing high concentrations of dissolved contaminants, migrates from tailing deposits into subjacent aquifers and finally enters adjacent streams (Hearne and Bush, 1996; Winde, 2001a;b). While off-site pollution by eroded slime particles can be prevented relatively easily and cost effectively (e.g. by covering slimes dams with vegetation), the same is not true for the aqueous pathway as experiences with rehabilitation of U mining sites in the USA (Robinson, 1995) and in Germany (Winde, 2002) show.

While a range of models exists to describe the transport of dissolved contaminants in groundwater (e.g. Wang et al., 2002, Cermakova et al., 2002) the same is not true for the associated diffuse contamination of streams and the subsequent downstream transport. Sediment-water systems through which U passes on its way from the slimes dams to the stream are schematically displayed in Fig. 1. The shallow aquifer developed within alluvial sediments of the floodplain associated with the stream is termed 'alluvial aquifer' (Seiler et al., 2002; Noseck et al., 2002) (Fig. 1).

This study aims to investigate both the hydrochemical behaviour of U while transported in solution as well as the hydrodynamics of the moving solution itself. Geochemical data are analysed in part I with respect to the mobility of U in different water-sediment systems along various aqueous pathways. Hydraulic relations between the stream and contaminated alluvial groundwater (as main source of diffuse stream pollution) are explored in the second part of this article series and diurnal and event-related fluctuations of stream-chemistry are analysed with regards to their implications for the mobility of dissolved U transported downstream in the third article of the series.

Study area

The Koekemoerspruit, located some 10 km west of Orkney in the North West Province, South Africa, is a tributary of the Vaal River and falls within the study area (Fig. 2).

It is a non-perennial stream with a total catchment area of about 815 km^2 at gauging station C2H139, which is operated by the Department for Water Affairs and Forestry (DWAF) (DWAF, 1999). With a mean annual precipitation (MAP) of approximately 600 mm, mainly occurring as intensive convectional rainfall during thunderstorms from December to March (summer), and a potential evapotranspiration of about 1 700 mm/a, the watershed yields a mean annual runoff of 9 million m^3 amounting to less than 2% of the MAP. Owing to highly permeable soils such as arenosols (covering 95% of the total catchment area) and lithosols (covering the remainder) in combination with only sparse vegetation (false grassveld type) (Middleton et al., 1981) retention in the catchment is low. Rainwater losses to the dolomitic bedrock, which partly forms the channel bottom of the Koekemoerspruit, also contribute to the low runoff. For securing safe and economically viable underground mining operations, the overlaying dolomitic aquifer is continuously dewatered by pumping dolomitic groundwater to the surface from a depth of 1 to 1.3 km at the closed-down Stilfontein gold-mine (Margaret shaft) through three to seven pumps.

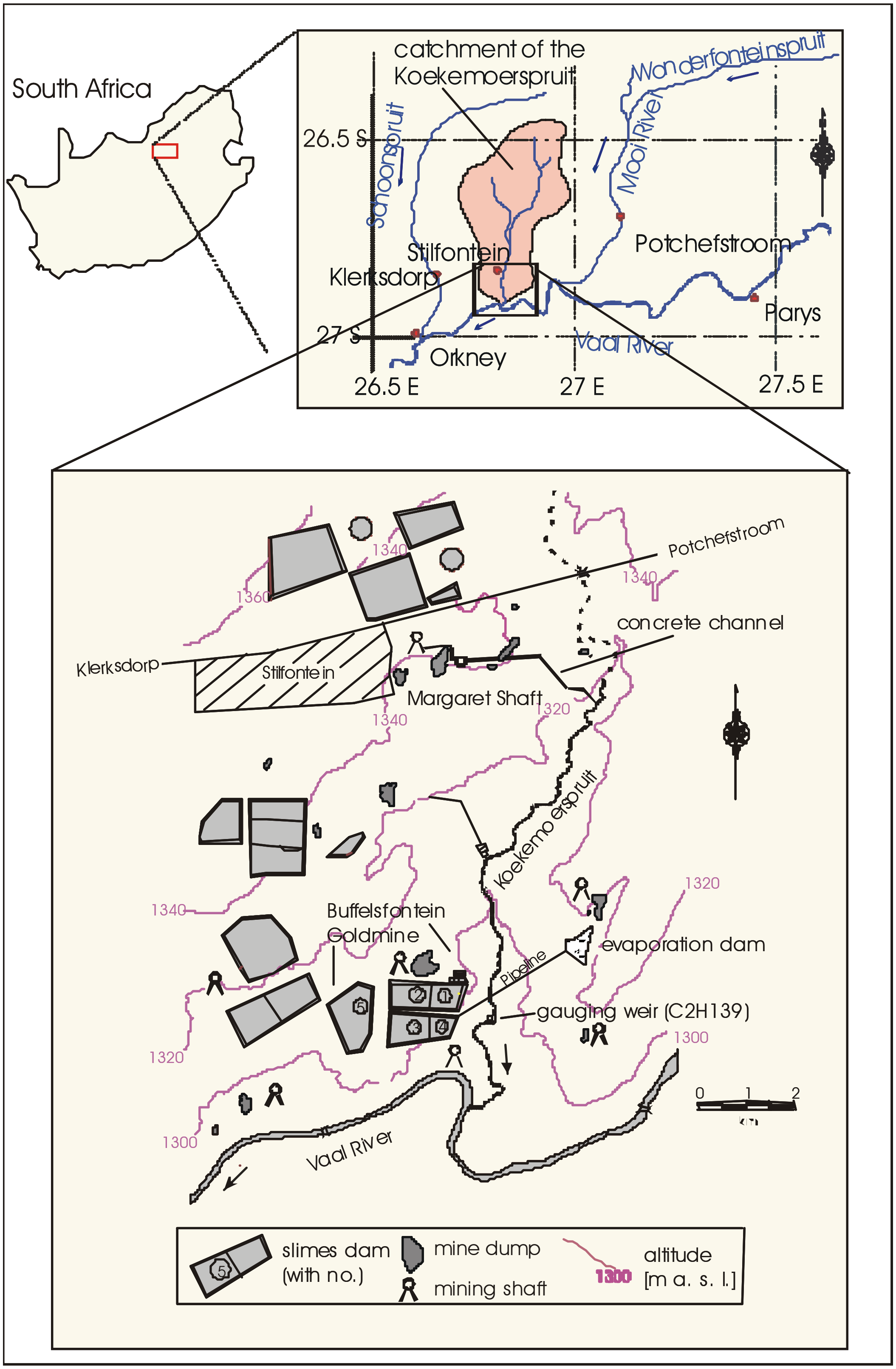

Figure 2
Study area

Depending on the number of pumps deployed the pumping scheme delivers a flow of 150 to 450 ℓ/s that is distributed to local farmers, industrial plants and irrigation schemes. The majority of the pumped water, however, is discharged via a concrete canal into the Koekemoerspruit where it sustains perennial flow for the remainder of the lower part of the stream. Computerised probes for water quality, gauging heights (stream and alluvial groundwater) and climatic parameters were installed at gauging station C2H139, some 9 km upstream of the confluence with the Vaal River, adjacent to several 20 m to 50 m high slimes dams of the Buffelsfontein Gold Mine (Fig. 2).

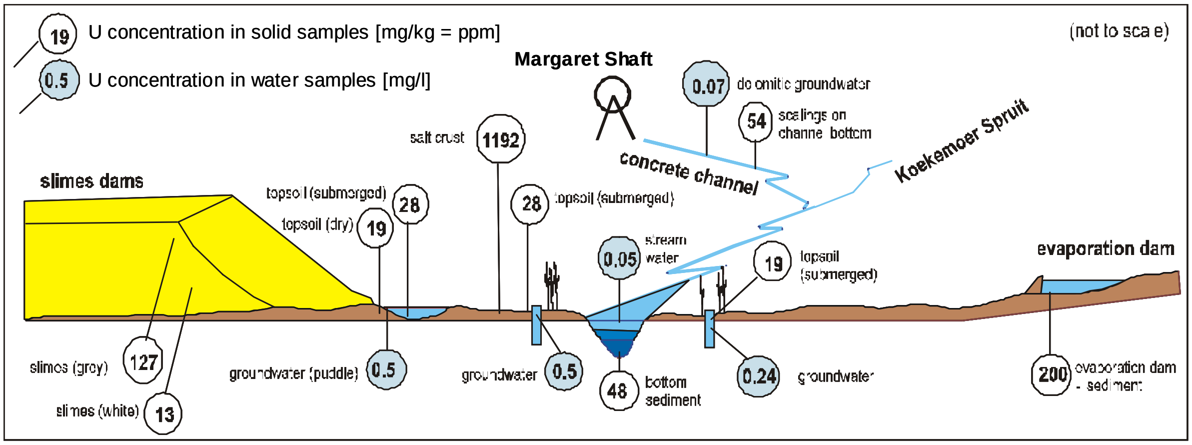

Figure 3

Simplified cross section through the floodplain of the Koekemoerspruit at gauging station C2H139 for illustrating the spatial distribution of uranium in water and sediments along the aqueous pathway

Aqueous pathways

Several unlined slimes dams of the Buffelsfontein Gold Mine are located about 500 m east of the Koekemoerspruit. Placed on well-draining dolomite they contain tailings from gold production as well as from combined gold and U production. With an average of 127 mg/kg U concentration found in mixed samples (n=4) the former contain about ten times the U concentration of tailings from combined gold and U production (13 mg/kg), which had been leached for the radioactive element. The U levels in both types of tailings are significantly above the regional background of about 2.5 mg/kg (CNS, 1996). Comprising about 150 million t of tailings the slimes dams cover an area of 2 500 ha (Winde, 2003).

A shallow aquifer developed in alluvial sediments of the approximately 400 m wide floodplain forms a hydraulic link between the slimes dams and the Koekemoerspruit. For slimes dam No. 4, which is some 38 m high, the piezometric head of the phreatic surface in the tailings is about 26 m above the average water level in the Koekemoerspruit (De Bruin, 2000). This results in a steep hydraulic gradient driving a permanent seepage flow towards the stream, as indicated by elevated groundwater levels in the partly submerged floodplain and high values for electrical conductivity (EC) in the groundwater.

Similar conditions are found on the left side of the stream (west) where an unlined evaporation dam designed for evaporating non-recyclable, highly contaminated process-water from the gold-mine acts as an additional source of groundwater contamination. Sediments on the bottom of the evaporation dam contain some 200 mg/kg U and are currently reworked for their gold content. Owing to the permeable dolomitic bedrock it has been estimated that only 1% of the disposed water actually evaporates, while the balance seeps into the underlying aquifer (Hearne and Bush, 1996). Although the hydraulic gradient on this side of the stream is considerably less steep, the drainage also migrates across the approximately 2 km-wide floodplain into the Koekemoerspruit.

Methods

Sediment and soil samples were collected as mixed samples from 2 to 3 spots of the upper 10 to 100 mm of the respective profile and the <2 mm fraction analysed for its *aqua regia* soluble content of heavy metals. The presence of U (as U_{nat}) was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), with a lower detection limit of 2 mg/kg. In water samples all other heavy metals were determined by mass spectroscopy (ICP-MS) while for analyses of solid samples atomic absorption spectroscopy (AAS) was used. U concentration in water samples was determined after filtration (0.45 µm) by laser-phosphorescence (lower detection limit: 0.001 mg/ℓ).

Results

The U concentrations as found in water and solid samples from different parts of the aqueous pathway are displayed in Fig. 3.

Discussion

General

U concentrations in various water – sediment systems along the identified aqueous pathways are interpreted below with respect to the mobility of U in different environments. In order to identify possible mechanisms of immobilisation correlations between U and other sediment constituents were performed, as well as distribution coefficients K_d between solute and solid phases of U analysed for selected systems of the aqueous pathway. Originally derived from batch experiments, the empirical concept of K_d values assumes that adsorption of dissolved contaminants onto sediment eventually equilibrates with the release from sediments back into the water. Although this is often not the case in highly energetic natural or semi-natural systems, K_d values are frequently used to assess the mobility of U in the environment (EPA, 1999). Defined as the ratio between metal concentration in solids and surrounding water, low K_d values indicate higher concentrations in the (mobile) water phase, i.e. the lower the K_d the higher the mobility of the metal in this water-sediment system and *vice versa* (BUNR, 1988; Van Cappellen and Wang, 1995). Important mechanisms for immobilising U in natural systems include the precipitation of U speciations with low solubility in water (e.g. Pourbaix, 1985; Shepherd and Cherry, 1992), the precipitation of salt crusts (hard pan formation) due to evaporation (Rammlemair, 2002), co-precipitation within the matrix of Fe and Mn oxihydroxides as coatings or gels (Markos and Bush, 1982; Jenne, 1995), co-precipitation with calcium carbonate (Hellmann, 1999) and pH-dependent adsorption onto negatively charged surfaces, e.g. of organic matter, clay minerals or freshly precipitated gels of iron hydroxides (Van Cappellen and

Wang, 1995; Luther, 1995). Influencing occurrence and intensity of all stated mechanisms (except for the evaporation-driven efflorescence of salts) the mobility of dissolved U is largely determined by the pH and Eh of the water. In general, acidic-oxidising conditions favour high U mobility, while moderate-alkaline and reducing conditions decrease the mobility of U (Pourbaix, 1985; Geipel et al., 1995). The solubility of U also depends on the oxidation-state of the ion, with tetravalent U (U^{4+}) being much less soluble than hexavalent U (U^{6+}, uranyl) (Geipel et al., 1995, Read and Falck, 1995). Other factors influencing the mobility of U include the ionic composition of the water (e.g. presence of salts for the formation of inorganic complexes), water temperature, atmospheric CO_2 pressure, contact time between water and sediment, grain size distribution of the sediment, water-sediment ratio and others (Fedoroff, 1998; BUNR, 1988; Geipel et al., 1995; Marcos and Bush, 1982). Sequential extractions used to simulate possible re-mobilisations of heavy metals from contaminated sediments usually target the associated four to five different sediment fractions in which U resides. Relevant natural processes of re-mobilising U from contaminated sediments include the desorption of U through replacement by other cations, oxidisation of reduced U species, reduction of iron and manganese hydroxides and dissolution of uraniferous carbonates (Förstner and Patchineelam, 1976; Wade et al., 2000).

U mobility in the alluvial groundwater - floodplain systems

Elevated U levels in the alluvial groundwater (0.24 to 0.54 mg/ℓ compared to 0.004 mg/ℓ as unweighted global mean for freshwater; DWAF, 1996) suggest that dissolved U is transported from slimes dams and the evaporation dam to the Koekemoerspruit. Almost identical U concentrations in groundwater samples (pH 7.8) throughout the floodplain on the side of the slimes dams indicate that surprisingly little U is retained by adsorption onto the highly sorptive floodplain sediments, as it is often found (Read and Falck, 1995; Winde, 2002). However, U concentrations in the topsoil of the floodplain being about ten times above the regional background simultaneously suggest that U does, to a certain extent, accumulate in alluvial sediments. This seems to be dependent on contact time, as higher U concentrations were found in "wet" soils (which have been submerged by groundwater while sampling) than in "dry" soils (28 mg/kg and 19 mg/kg respectively).

Extremely high concentrations of U occurred in salt crusts, which had formed on the surface of floodplain sediments in slightly elevated positions in the micro-relief. At 1192 mg/kg, their U concentration is almost ten times higher than the maximum concentration found in the tailings. Such crusts form when capillary-ascending groundwater evaporates and dissolved sulphates, which mainly originate from pyrite oxidation and sulphuric acid leaching, commonly precipitate as gypsum, epsomite or gosslarite (Robinson, 1995; Markos and Bush, 1982; Rammlemair, 2002). With groundwater on this side of the stream displaying a redox-potential well above -400 mV (-100 mV to -270 mV decreasing with depth), it is likely that the extraordinarily high U content of such crusts is due to the formation of neutrally charged uranyl sulphate complexes, which are often found in sulphate-dominated waters of such redox-potential (Markos and Bush, 1982, Seiler et al., 2002). Elevated concentrations of dissolved carbonates in the groundwater originating from dolomite may also allow for aqueous uranyl carbonate complexes (Seiler et al., 2002) or the calcium uranium carbonato complex $\{Ca_2[UO_2(CO_3)_3\}$ to form, with the latter pointing to the importance of calcium concentrations in affected waters (Geipel et al., 1995). Being neutral or negatively charged, such complexes may prevent U from being adsorbed onto negatively charged surfaces of alluvial sediments and explain the unexpected low U retention (Payne, 1998). Owing to high evaporation rates and elevated water tables near slimes dams, crust formation is rife and of particular concern after longer dry periods, when the first flush of runoff into streams becomes particularly polluted. Not fenced and freely accessible, e.g. for cattle grazing, such salt crusts constitute a potential entrée point for U into the food chain and a health hazard. Sulphate crusts were also observed at capillary fringes in bank sediments of the stream canal. If stream levels fluctuate (as they do in the Koekemoerspruit) these crusts may dissolve periodically, releasing U pulses into the stream.

U mobility in the water-sediment system of the concrete canal

The dolomitic groundwater pumped from the closed Stilfontein gold-mine is discharged into the Koekemoerspruit via a concrete canal. While the U concentration in this water is almost ten times lower than in the alluvial aquifer, with 50 to 60 mg/kg the U concentrations of sediments in the concrete canal (which are better described as scales) and the stream (mainly sand and gravel) is significantly higher than that in the floodplain.

Comparing K_d-values for the floodplain - groundwater system with those in the stream and the concrete canal, surprisingly a significantly lower mobility for U in the latter was found, despite much faster flowing water and significantly shorter sediment - water contact time than in the groundwater systems. In both systems, the concrete canal and the stream channel, precipitation processes were identified as a likely cause of this low U mobility.

With >74 wt% of $CaCO_3$ the canal scales mainly consist of precipitated carbonates, explaining the scaly nature of the sediment. Since dolomitic groundwater is highly saturated with Ca^{2+} and CO_3^{2-}, de-calcification readily occurs. Hellmann (1999) found for the River Rhine (Germany) that this process, triggered by photosynthesis of algae and green aquatic plants, constitutes an important mechanism of removing dissolved heavy metals from the water column. A strong correlation between U concentration and $CaCO_3$ content in sediment samples (correlation coefficient, R = 0.82; 8 samples) suggests that this mechanism also occurs in the study area. The increase of the correlation factor R to 0.84 when the two soil samples are left out suggests that carbonate-precipitation is more dominant in the concrete furrow and the Koekemoerspruit than it is in the floodplain.

U mobility in the water-sediment system of the stream

Carbonate precipitation, however, does not explain the relatively high U concentration in sand and gravel from the bottom of the stream canal, which contains only small amounts of $CaCO_3$. Located where highly contaminated groundwater from the floodplain seeps into the stream canal, bottom sediments are prone to be contaminated by redox-controlled precipitation. While groundwater constitutes a reducing environment, turbulently flowing stream water is well oxygenated. Due to mixing within the pores of the bottom sediments dissolved Fe(II) and Mn(II) of the groundwater become oxidised and precipitate, partly catalysed by bacteria, as Fe(III) and Mn(IV) hydrous oxides and hydroxides (FeOOH, $Fe(OH)_3$). The products of these precipitation processes are amorphous gels settling in sediment pores and so-called 'coatings' covering the surface of solid sediment particles (Busch, 1988). Over a period of several weeks the water-saturated gels gradually crystallise into water-free oxides (Fe_2O_3, hematite), which then becomes a genuine solid constituent of the sediment, often cementing sediment particles (Mattheß, 1990). A strong correlation in solid samples between the concentrations of U and iron (R = 0.97) as well as between U and manganese (R = 0.91) suggests that these processes are important mechanisms of U immobilisation in the study area.

The removal of U^{6+} from the water phase either occurs by incorporation of U in the matrix of precipitating oxyhydrates (Noubactep et al., 2002) or by adsorption onto the large reactive surface of freshly precipitated gels (Mallants et al., 2002). However, strong correlations of U with most of the heavy metals in the sediments (except for Cr/Ni all heavy metals correlate with U at R > 0.90; n = 8-12) suggest that (unspecific) co-precipitation dominates over (selective) adsorption according to valency and ion-size. Since seepage from tailings deposits usually contains high concentrations of dissolved Fe^{2+} and Mn^{2+}, a fairly high amount of both metals is available for removing U by precipitating as hydroxides as soon as oxygen becomes available.

The formation of uraniferous coatings on the surface of particles also explains how U can be retained even in coarse sediments, which have almost no sorption capacity. In sediments where such coatings are the main cause of U contamination, concentrations increase with decreasing grain-size of the sediment. This is due to the fact that the surface of approximately spherical particles relatively increases compared to the volume with the smaller the diameter of the particles are. With a higher surface area per mass-unit covered by uraniferous coatings this results in higher U concentrations. This purely geometrical effect needs to be taken into consideration when U concentration in sediments is used for indirectly assessing previous water pollution (Winde, 2003).

Located at the interface between reducing groundwater and oxidising streamwater, bottom sediments constitute a geochemical barrier where U and other heavy metals are removed from groundwater that seeps into the stream canal. Protecting freshly precipitated gels inside the pores from fluvial erosion bottom sediments also act as long-term sinks for U and other heavy metals and reduce downstream pollution thereby.

Conclusion

The results suggest that transport of dissolved U from slimes dams is a major pathway for environmental contamination of stream water, groundwater and sediments. In contrast to erosion of U bearing particles, were U is 'diluted' by uncontaminated material along the pathway, solute transport is associated with chemical re-concentration of U in the environment. Such secondary accumulations often occur well away from the mining property in unprotected areas with different land use, and frequently display U levels which may exceed concentrations in the original sources of contamination. U precipitation processes in flowing surface water rather than adsorption onto floodplain sediments from groundwater determine the extent of diffuse stream contamination. Since immobilisation processes are highly dependent on pH and Eh, immobilisation preferably occurs where chemical conditions change significantly. This happens either at interfaces between different geochemical compartments along the aqueous pathway (e.g. bottom sediments) or within compartments due to temporal fluctuations of chemical conditions. The dynamics of the latter in stream water and implications for the downstream transport of U are analysed in the third part of this article series (Winde et al., 2004).

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References

BUNR (BUNDESMINISTER FÜR UMWELT, NATURSCHUTZ UND REAKTORSICHERHEIT) (1988) Radionuklide in Wasser-Schwebstoff-Sediment-Systemen und Abschätzung der Strahlenexposition. Fischer Verlag, Stuttgart, New York. 300 pp.

BUSCH KF (1988) *BI-Taschenlexikon Wasser*. Leipzig.

CERMAKOVA H, NOVAK J and MUZAK J (2002) Application of numerical system on Turonian aquifer remediation control. In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *U in the Aquatic Environment*. Berlin, Heidelberg. 323-330

COLE DI (1998) Uranium. In: Wilson MGC and Anhaeusser CR (eds.) *The Mineral Resources of South Africa*. Handbook, Council for Geoscience, **16** 642-652

CNS (COUNCIL FOR NUCLEAR SAFETY) (1996) Report on radioactive contamination at New Machavie gold mine on the farm Eleazer 377 IP, Magisterial district of Klerksdorp. DWAF Potchefstroom.

DE BRUIN P (2000) Personal communication. Water Manager, Buffelsfontein Gold Mine. July 2000.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY) (1996) *South African Water Quality Guidelines*. Vol **1**: *Domestic Water Use*. Pretoria.

DWAF (DEPARTMENT FOR WATER AFFAIRS AND FORESTRY) (1999) Water Quality Data of Station C2H139. Data catalogue, Pretoria.

EPA (ENVIRONMENTAL PROTECTION AGENCY, OFFICE OF AIR AND RADIATION) (1999) Understanding variation in partition coefficient, K_d values. EPA report no 402-R99-004A. Washington.

FEDOROFF M (1998) Sorption mechanisms of heavy metal ions and role of sorption - Desorption in their transport in water. Abstract in http://www.geo.TU freiberg.de/umh/abstracts.doc.html. Accessed: 24.08.1999.

FORD MA (1993) Uranium in South Africa. *J. S. Afr. Inst. Min. Metall.* **93** (2) F February 1993. 37-58.

FÖRSTNER U and PATCHINEELAM SR (1976) Bindung und Mobilisation von Schwermetallen in fluviatilen Sedimenten. *Chemikerzeitung* **100** (2) 49-57.

FUNKE JW (1990) The Water Requirements and Pollution Potential of South African Gold and U mines. WRC Report No. KV 9/90, Pretoria. 172 pp.

GEIPEL G, BERNHARD G, BRACHMANN A, BRENDLER V, NITSCHE H (1995) Speziation des Us in Haldensickerwässern des Uranbergbaus. In: Merkel B; Hurst S; Löhnert EP, Struckmeier W (eds.) *U Mining and Hydrology*. *Proc. Int. Conference and Workshop in Freiberg*, Germany, October 1995. GeoCongress I, Köln, 167-175.

HEARNE CL and BUSH RA (1996) Investigation into the impact of diffuse seepage from gold-mines in the Klerksdorp region on water quality in the Vaal River, Phase 1. Report No. CED/011/96 for the Klerksdorp Mine Managers Association (KMMA). Johannesburg. Unpublished.

HELLMANN H (1999) *Qualitative Hydrologie – Wasserbeschaffenheit und Stoff-Fluesse*. Berlin-Stuttgart.

IWQS (INSTITUTE FOR WATER QUALITY STUDIES, DWAF) (1999) Report on the radioactivity monitoring programme in the Mooi River (Wonderfonteinspruit) catchment. Report No. N/C200/00/RPQ/2399.

JANISCH PR (1986) Gold in South Africa. *J. of the S. Afr. Inst. of Mining and Metallurgy* **86** (8) 273-316.

JENNE EA (1995) Metal adsorption onto and desorption from sediments: I. Rates. In: Allen HE (ed.) (1995) *Metal Contaminated Aquatic Sediments*. Ann Arbor Press, Inc., Michigan. 81-105.

LUTHER GW (1995) Trace metal chemistry in porewaters. In: Allen HE (ed.) (1995) *Metal Contaminated Aquatic Sediments*. Ann Arbor Press, Inc., Michigan, 65-75.

MALLANTS D, DIELS L, BASTIEANS L, VOS J, MOORS H, WANH L, MAES N and VANDENHOFE H (2002) Removal of U and arsenic from groundwater using six different reactive materials: assessment of removal efficiency. In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment*. Berlin, Heidelberg, 565-573.

MARKOS G and BUSH KJ (1982) Geochemical processes in uranium tailings and their relationship to contamination. In: IAEA (ed.) *Management of Waste from Uranium Mining and Milling*. Wien. 231-246.

MATTHEß G (1990) *Lehrbuch der Hydrogeologie. Vol. 2: Die Beschaffenheit des Grundwassers*. Berlin, Stuttgart. 483 pp.

McLEAN CS (1994) The uranium industry of South Africa. *J. S. Afri. Inst. Min. Metall.* 113-122.

MIDDLETON BJ, PITMAN WV and MIDGLEY DC (1981) *Surface Water Resources of South Africa. Vol II: Drainage Region C, The Vaal Basin. Part 1 (Text), Part 2 (Appendices)*. WRC-Report No. 8/81. Pretoria

NOSECK U, BRASSER T, LACIOK A, HERCIK M and WOLLER F (2002) Uranium migration in argillaceous sediments as analogue for transport processes in the far field of repositories (Ruprechtov site, Czech Republic). In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment*. Berlin, Heidelberg, 211-220.

NOUBACTEP C, MEINRATH G, VOLKE HJ, DIETRICH P and MERKEL BJ (2002) Mechanisms of uranium fixation by zero valent iron: The importance of co-precipitation. In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment*. Berlin, Heidelberg. 581-590.

PAYNE TE (1998) Uranium sorption on tropical wetland sediments. Abstract in http://www.geo.tU freiberg.de/umh/abstracts.doc.html. Accessed 24.08.1999.

POURBAIX M (1985) *Atlas of Electrochemical Equilibria in Aqueous Solutions.* Houston, Brussles. 208-210.

RAMMLEMAIR D (2002) Hard pan formation on mining residues. In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment.* Berlin, Heidelberg. 177-186.

READ D and FALCK WE (1995) Long-term uranium migration behaviour – An overview of the natural analogue studies carried out in the British isles. In: Merkel B, Hurst S, Löhnert EP and Struckmeier W (eds.) *Uranium Mining and Hydrology. Proc. Int. Conf. Workshop in Freiberg*. Germany, October 1995. GeoCongress, Köln.

ROBB LJ and ROBB VM (1998a) Environmental impact of Witwatersrand gold mining. In: Wilson MGC and Anhaeusser CR (eds.) *The Mineral Resources of South Africa: Handbook, Council for Geoscience.* **16** 14-16.

ROBB LJ, ROBB VM (1998b): Gold in the Witwatersrand basin. In: Wilson MGC and Anhaeusser CR (eds.) *The Mineral Resources of South Africa: Handbook, Council for Geoscience*. **16** 294-349.

ROBINSON WP (1995) Groundwater contamination at uranium mill sites in the United States reclaimed by the Department of Energy (DoE) Uranium Mill Tailings Remedial Action Project (UMTRAP): a review of seven selected sites. In: Merkel B, Hurst S, Löhnert EP and Struckmeier W (eds.) *Uranium-Mining and Hydrology. Proc. Int. Conf. Workshop in Freiberg*. Germany, October 1995. GeoCongress, Köln.

SEILER KP, GRAF W, LANG H and ZAPATA R (2002) Groundwater flow systems and the export of uranium from nuclear waste repositories to the biosphere. In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment*. Berlin, Heidelberg. 221-230.

SHEPHERD TA and CHERRY JA (1992) *Schadstofftransport in Sickerwässern von Uran-Tailings-Deponien: Ein Überblick. Buergerinitiative gegen Uranabbau im Südschwarzwald [Hrsg.]: Sanierung von Altlasten des Uranbergbaus, Materialsammlung*. 55-77.

TUREKIAN T and WEDEPOHL H (1961) Distribution of the elements in some major units of the earth's crust. *Geol. Soc. of Am. Bull.* **72**1 75-192.

VAN CAPPELLEN P and WANG Y (1995) Metal cycling in surface sediments: Modelling the interplay of transport and reaction. In: Allen HE (ed.) *Metal Contaminated Aquatic Sediments.* Michigan, 21-60.

VENTER I (2001) South African mining sector facing radiation challenge. *Mining Weekly* **7** (43) 9-15.

WADE PW, WOODBOURNE S, MORRIS WM, VOS P and JARVIS NV (2000) Tier 1 Risk Assessment of Radionuclides in Selected Sediments of the Mooi River. WRC-Project No K5/1095. 93 pp.

WANG Y, MA T and LECHANG X (2002) A 3-D numerical modelling of reactive transport of U(VI) in shallow groundwaters: a case study at a uranium mill tailings site in southern China. In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment*. Berlin, Heidelberg, 307-314.

WENDEL G (1998) Radioactivity in mines and mine water – Sources and mechanisms. *J. S. Afr. Inst. Min. Metall.* (March/April) 87-92.

WINDE F (2001a) Fluvial processes and uranium transport – Pitfalls from the Wismut region (Germany) and the Klerksdorp gold field (South Africa). *Proc. 4th Int. Conf. Soc. S. Afr. Geographers.* Goudini Spa, 3-6.7.2001, CD.

WINDE F (2001b) Slimes dams as source of uranium-contamination of streams – The Koekemoerspruit (Klerksdorp Gold-field) as a case study. *Proc., Chamber of Mines of South Africa (2001): Conference on Environmentally Responsible Mining in Southern Africa*. Muldersdrift/Johannesburg, 25-28 September 2001, Vol. 1, 2C-1 – 2C-10.

WINDE F (2002) Fluviale Prozesse und Urantransport – Beispiele aus der Wismutregion Ostthüringens und den Goldbergbaugebieten Südafrikas. In: *Trierer Geographische Studien*, Heft **25** 47-64.

WINDE F (2003) Urankontamination von Fließgewässern – Prozessdynamik, Mechanismen und Steuerfaktoren. Untersuchungen zum Transport von gelöstem Uran in bergbaulich gestörten Landschaften unterschiedlicher Klimate. Habilitationsschrift, Universität Jena. 377 pp.

WINDE F and DE VILLIERS AB (2002a) The nature and extent of uranium contamination from tailings dams in the Witwatersrand gold mining area (South Africa). In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment.* Berlin, Heidelberg. 889-897.

WINDE F and DE VILLIERS AB (2002b) U contamination of streams by tailings dams – Case studies in the Witwatersrand gold mining area (South Africa). In: Merkel BJ, Planer-Friedrich B and Wolkersdorfer C (eds.) *Uranium in the Aquatic Environment.* Springer Berlin, Heidelberg, 803-812.

WINDE F, WADE P, VAN DER WALT IJ (2004) Gold tailings as a source of water-borne stream contamination – The Koekemoerspruit (Klerksdorp gold field, South Africa) as a case study. Part III of III: Fluctuations of stream chemistry and their impacts on U mobility. *Water SA* **30** (2) 233-240.

WYMER D (2001) The impact of gold mining on radioactivity in water and foodstuffs. *Proc., Chamber of Mines of South Africa (2001): Conference on Environmentally Responsible Mining in Southern Africa.* Muldersdrift/Johannesburg, 25-28 September 2001, Vol. **1**, 2C-19 – 2C-30.