URANIUM CONTAMINATION OF FLUVIAL SYSTEMS – MECHANISMS AND PROCESSES

PART I: GEOCHEMICAL MOBILITY OF URANIUM ALONG THE WATER-PATH – THE KOEKEMOERSPRUIT (SOUTH AFRICA) AS A CASE STUDY

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ABSTRACT: Tailings deposits from gold- and uranium mining usually contain elevated amounts of radioactive and chemotoxical heavy metals. By seepage dissolved uranium and other contaminants migrate from tailings deposits via groundwater into adjacent fluvial systems. The subsequent transport in streams and rivers is one of the most effective pathways of distributing contaminants throughout the biosphere. In a comparative study of mining areas in Germany, South Africa and Australia mechanisms of non-point stream-contamination and the aqueous transport of uranium were investigated. The study comprises geochemical analyses of samples from various sediment-water systems along the aqueous pathway as well real-time in situ-measurements in the fluvial system itself.

In this paper geochemical data of water- and sediment samples from the Koekemoer Spruit as a typical example for a mining affected stream in South Africa - are analysed with respect to possible mechanisms of transport and immobilisation of uranium migrating in solution. Ratios between dissolved and solid phases of uranium for various water-sediment-systems along the aqueous pathway indicated, unexpectedly, significant lower mobility of uranium in stream and channel water than in the groundwater-floodplain system. Correlation of various geochemical parameters suggests co-precipitation of uranium along with calcium-carbonate and iron/manganese-compounds is the main reason for the higher immobilisation rate in the flowing water systems.

RESUMEN: Las escombreras de la minería de oro y uranio contienen elevadas cantidades de metales pesados radioactivos y tóxicos. Por infiltración el uranio disuelto y otros contaminantes migran hacia los sistemas fluviales próximos. El transporte fluvial es uno de los sistemas más eficaces de distribución de contaminantes en la biosfera. En un estudio comparado de áreas mineras de Alemania, Sudáfrica y Australia se investiga-

*ron los mecanismos de contaminación difusa y transporte hídrico de ura -
nio. El estudio comprende análisis geoquímicos de muestras de agua y
sedimento y en tiempo real a lo largo de un sistema fluvial.*

*En este trabajo se analizan datos de agua y sedimento del Koekemoer
Spruit como ejemplo de río afectado por minería en Sudáfrica, en relación
con posibles mecanismos de transporte e inmovilización de uranio disuel -
to. Las relaciones entre fases disueltas y sólidas de uranio a lo largo del
sistema fluvial indican, sorprendentemente, una menor movilidad del ura -
nio en el cauce que en el sistema subterráneo. La correlación entre varios
parámetros geoquímicos sugiere que la coprecipitación de uranio, carbo -
nato cácico y compuestos de hierro y manganeso es la prinicpal razón de
la elevada tasa de inmovilización en el cauce.*

1. Introduction

Uranium is a radioactive heavy metal, which is widely dispersed throughout the
earth's crust, with an average concentration in rocks and soils of 2-4 mg/kg (ppm).
However, in the auriferous sediments of the Witwatersrand uranium is accumulated up to
1000ppm, displaying average concentrations of about 100ppm. Compared to ore with U-
grades of 3-6% mined in Canada and Australia this is regarded as low-grade ore (CfG,
1998). Therefore in South Africa uranium was mainly produced as a by-product of gold,
which already covers the mining costs. Between 1952 - when the first regular U-recov-
ery plant was commissioned - and 1991 a total of 167,000t of U_3O_8 was produced
(Waggitt, 1994). After a peak in production in 1980 (6000t U_3O_8) the uranium price on
the world market and subsequently the U-production in SA steadily declined. From 26
mines, which at one stage were feeding into 18 uranium recovery plants currently in 1995
only 3 mines and 4 plants are left, producing about 1500t U_3O_8 per year (CfG, 1998).

Due to the much lower gold content in the ore compared to uranium excessive
amounts of uranium are brought to the surface (and thus into the biosphere) by gold
mines. After milling and leaching the remaining ore-material (tailings) is deposited as a
solid-water-mixture on so called „slimes dams". Uranium is present mainly in slimes
dams which were deposited before the uranium production in South Africa was started or
in those where the milled ore, for economic reasons, was never leached for uranium. Due
to the decline of the U-production in many slimes dams uranium levels are rising. Since
sulphuric leaching (as most commonly used technology in SA) extracts some 90% of the
original U-content an increase of uranium concentrations in slimes dams by factor 10 is
to be expected. Since former uranium producing mines mainly used ore with U-grades
above average this increase results in particularly high conentrations. Comparing the
maximal production rate in 1980 with the present one a difference of about 4500t urani-
um per year results, which is additionally dumped on slimes dams. With slimes dams in
the goldfields of the Witwatersrand basin covering an area of about 400km[2] and contain-
ing some 430,000t U_3O_8 they constitute an environmental problem of extraordinary spa-
tial dimensions (CfG, 1998: Winde, 2001).

While off-site pollution with contaminated tailing particles from the slimes dams by water- and wind erosion can be prevented comparativly cost effective (e.g. vegetation cover) the same is not true for the seepage-related transport of dissolved contaminants. The assumption that the negative annual water balance in gold mining areas prevents seepage (Funke, 1990) is contradicted by a number of more recent studies (Hearne & Bush, 1996, Winde, 2001). The contamination of streams by adjacent slimes dams poses a particular risk for the health of people in informal settlements where polluted stream water often is consumed without appropriate treatment. But also long term effects on cattle and crop farming and established drinking water supply schemes are of concern as a number of recently launched projects show (e.g. IWQS, 1999; Wade *et al.,* 2000).

While the majority of said projects focus on uranium concentration in water and sediments in comparison to legislation limits, this study concentrates on hydrochemical and hydrodynamic mechanisms of diffuse stream contamination. Whereas this paper, as part I of III, analyses geochemical data with respect to the mobility of uranium along the aqueous pathway in part II the hydraulic relations between the alluvial groundwater and the stream are explored. In the last part, diurnal and event-related fluctuations of the stream-chemistry are analysed with respect to implications for the downstream transport of dissolved uranium once it has entered the fluvial system.

2. Study area

The Koekemoer Spruit, located near Orkney in the North West Province, is a tributary of the Vaal River (Figure 1). The size of the catchment area is about 860km^2. Due to the small volume of runoff, which equals less than 2% of the annual rainfall, the Koekemoer Spruit shows only seasonal flow. However, the Koekemoer Spruit is also fed by pumped groundwater from the closed Stilfontein Goldmine. The pumping scheme is in operation to prevent the adjacent Buffelsfontein mine from being flooded and sustains a perennial flow of 150-450l/s.

The study area comprises a cross-section through the floodplain of the stream near a gauging weir from the DWAF (C2H139), stretching from slimes dams on the right hand stream bank to an evaporation dam on the left hand stream bank. The unlined slimes dams of the Buffelsfontein Gold mine are regarded as the most important sources of uranium contamination in the study area. A shallow alluvial aquifer in the floodplain constitutes a hydraulic link between the slimes dams and the Koekemoer Spruit. For slimes dam No #3, which is some 38m high, the piezometric head is about 26m above the average water level in the Koekemoer Spruit (De Bruin, 2000). The resulting hydraulic gradient drives a permanent water flow to the stream, as high levels of groundwater with elevated electric conductivity (EC) in the floodplain suggest. The direction of flow is slightly modified by a weak down-valley gradient towards the Vaal River.

Similar conditions were found on the left-hand side of the stream although the hydraulic gradient is less steep. Here an evaporation pan dam, which is designed for evaporating non-recyclable process-water from the gold mine, acts as source of ground-
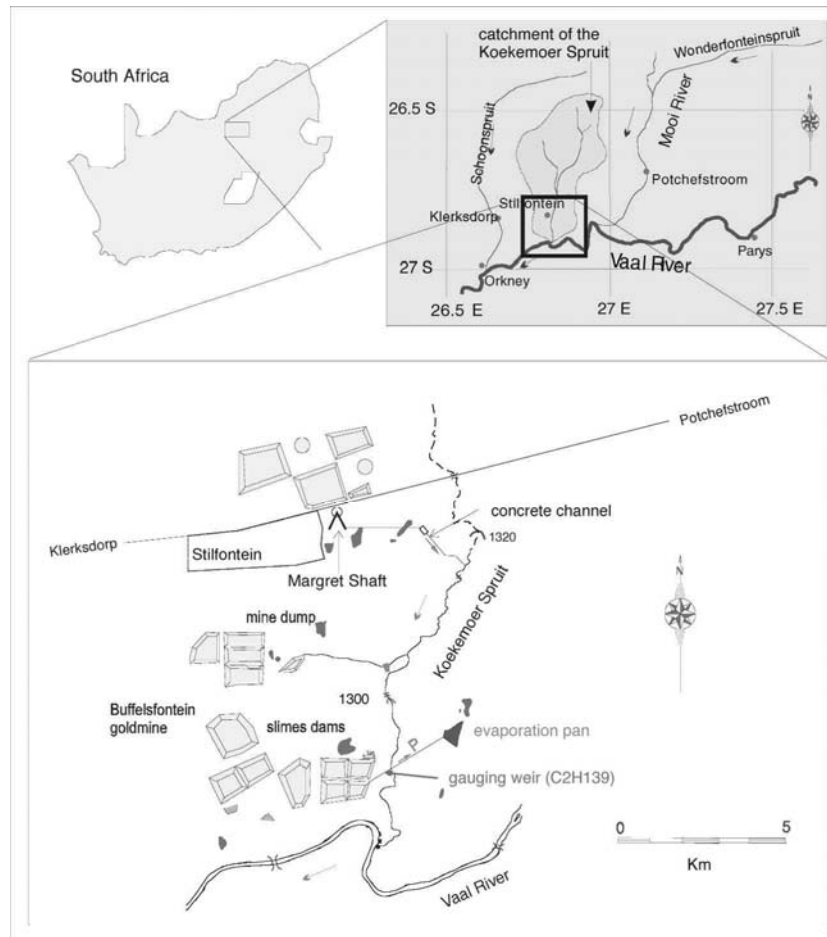
Figure 1. Study area

water contamination. Because of the highly permeable dolomitic underground, it has been estimated that <2% of the disposed water really evaporates, while the remaining balance seeps into the underground (Hearne & Bush, 1996).

3. Methods

Sediment and soil samples were collected from the upper 1-3cm below surface and analysed for aqua regia soluble content of heavy metals. Chemical uranium (U_{nat}) was analysed by ICP-OES (Inductive Coupled Plasma Optical Emission Spectrometry), with

a lower detection limit of 2ppm. All other heavy metals were determined by ICP-MS (Inductive Coupled Plasma Mass Spectroscopy). Water samples were filtrated (0.45um) and analysed for U_{nat} by Llaser-phosphorescence (lower detection limit: 0.001ppm). All other heavy metals were determined by ICPMS.

4. Results

The uranium concentration in water – and solid samples alongside the aqueous pathway are displayed in Figure 2.
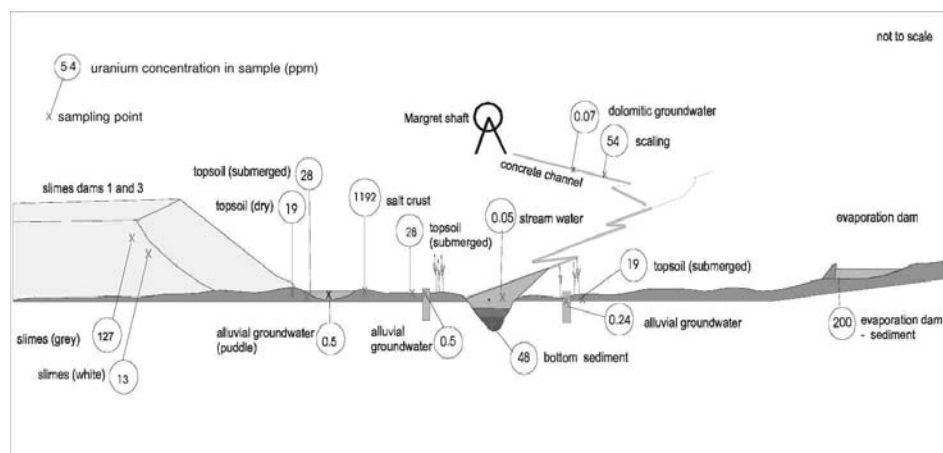

Figure 2. uranium concentrations (ppm) in solid- and water samples from the Koekemoer Spruit alongside the aqueous pathway.

5. Discussion

5.1. Uranium Mobility in the Alluvial Groundwater-Floodplain System

Uranium concentrations prove that aqueous uranium transport from the slimes dams and the evaporation dam to the Koekemoer Spruit takes place. With 13ppm U in material from the slimes dam an example for tailings from which U was extracted was sampled. The much higher concentration in more recent deposited tailings, however, reflects the tenfold increase of the uranium levels after uranium extraction was abandoned. With about 50 times above the natural background of uranium in the area (2.5ppm) the slimes dams constitute a significant source of pollution. The same is true for sediment in the evaporation pan that contains 200ppm U.

While sampling of pure seepage was not possible, the elevated level of uranium in the alluvial groundwater (about 0.5ppm) clearly indicates a solute transfer of uranium from the slimes dams. Identical uranium concentrations in groundwater samples throughout

the floodplain suggest that no significant retention of the dissolved uranium by adsorption onto the highly sorptive floodplain sediments takes place as often described for other areas (Read & Falck, 1995; Payne, 1998, Winde, 2000). However, elevated uranium contents of the topsoil in the floodplain which are about ten times above regional background indicate that dissolved uranium from the groundwater does accumulate in the sediments to a certain extent. This seems to increase with contact time as higher concentration of "wet" soils (which have been submerged by groundwater while sampling) compared to "dry" soil suggests (28ppm to 19ppm respectively).

Extremely high concentrations of uranium were found in salt crusts, which had formed on the surface of floodplain sediments in slightly elevated positions in the micro relief. At 1192ppm, their uranium concentration is almost ten times higher than the maximum concentration found in the tailings. Such crusts form when capillary-ascending groundwater evaporates and the containing sulphates commonly precipitate as gypsum, epsomite or gosslarite. The extraordinary high uranium content of such crusts is likely to be due to the formation of uranyl-sulphate-complexes ($UO_2(SO_4)_x^{y-}$; $x=1,2,3$; $y=0,2,4$), which are often found in sulphate-dominated waters (Markos & Bush, 1982). The incorporation of the cation uranium in such neutral complexes prevents it from binding onto negatively charged adsorbents in the sediments, simultaneously explaining the low retention of groundwater transported uranium in the floodplain. Due to their high solubility such crust are easily re-soluted by rainwater. Especially with surface run off from rainfall after longer dry periods dissolved uranium is likely to be flushed into the stream. Capillary fringes with sulphate precipitation also were observed in bank sediments of stream channels. I.e. fluctuating gauging heights in the stream, e.g. caused by changing pumping rates, are likely to re-solute those crusts, which may result in pulses of dissolved uranium in stream water.

The fact that the uranium concentration in the floodplain on the left-hand side of the stream is almost the same as in those of the right-hand side (19ppm) despite a significantly lower solute concentration in the alluvial groundwater (only 50%) points to an additional binding mechanism. Uranium, like iron, manganese and vanadium, is one of the few metals where the solubility depends on the oxidation-state of their ions (Matthes, 1990). Since the redox-potential of groundwater in the left-hand aquifer is much more reducing than in the right-hand aquifer (–250mV) reduction of the uranyl-ion to its tetravalent form (U^{4+}), which has significant lower solubility, may be an additional possible mechanism of immobilisation.

5.2. Uranium mobility in the Dolomitic groundwater – scaling System of the concrete channel

While the uranium concentration in the dolomitic groundwater, which via a concrete channel also feeds the Koekemoer Spruit, is almost ten times lower than in the alluvial aquifer the uranium contents of the sediments in the concrete channel and in the stream is significant higher than in the floodplain (50-60ppm).

To compare the mobility of uranium in different sediment-water systems with each other, distribution coefficients (Kd) were calculated. Since Kd is defined as the ratio between metal concentration in the solids and the water, low values indicate high concentrations in the (mobile) water phase i.e. high metal mobility and vice versa. Comparing Kd-values for the floodplain-groundwater system with the stream and the concrete channel, a significant lower mobility for uranium in the latter ones was unexpectedly found. Apart from adsorption onto negatively charged substances like clay minerals and organic material, dissolved uranium also can be immobilised by precipitation out of the water column. With a content of > 74wt% of $CaCO_3$ the (greyish) channel scaling suggests that they are mainly the results of carbonate precipitation. Since dolomitic groundwater is highly saturated with Ca^{2+} and CO_3^{2-} photosynthesis triggered precipitation of $CaCO_3$ (biological decalcification) readily occurs. Hellmann (1999) found for the river Rhein (Germany) that decalcification caused by algae and green water plants constitutes an important mechanism of removing dissolved heavy metals from the water column.

A high correlation between the uranium concentration and the content of $CaCO_3$ in sediment samples (R=0.82; n=8) suggests that this process also takes place in the study area. The increase of the correlation factor R to 0.84 when soil samples are left out (n=6) indicates that carbonate precipitation is more dominant in the concrete furrow and the Koekemoer Spruit than in the floodplain.

5.3. Uranium mobility in the Streamwater – bottom sediment system

However, this mechanism cannot explain the high uranium concentration found in the stream sediment, which only contains small amounts of $CaCO_3$. Since the samples were taken where highly contaminated groundwater from the floodplain seeps through the bottom sediment, a redox-controlled mechanism of uranium immobilisation is more likely to occur. While the almost oxygen-free groundwater constitutes a reducing environment, the turbulently flowing stream water usually contains higher concentrations of dissolved oxygen and shows oxidising conditions. Due to mixing processes in the interstitial of the bottom sediments, the dissolved Fe(II) and Mn(II) in the groundwater becoming oxidised and precipitate, partly catalysed by bacteria, as Fe(III) and Mn(IV)hydrous oxides (e.g. iron-ochre, birnesite, braunstein) resp. –hydroxides (FeOOH, $Fe(OH)_3$). They form either amorphous gels in the pores or coatings on solid sediment particles (Busch, 1988). Over a period of several weeks the water-saturated Fe(III)hydroxide gel gradually crystallises into water-free oxide (Fe_2O_3: hematite), which then becomes a genuine solid constituent (Matthes, 1990). A strong correlation between the uranium concentration in the solid samples and the content of iron (R=0.97) and manganese (R=0.91), which further increases when the Fe and Mn concentrations are added (R=0.98), suggest that these processes are important mechanisms of uranium immobilisation in the study area.

The extraction of uranium from the water phase either happens by co-precipitation or subsequent adsorption onto the large reactive surface of the freshly precipitated

iron(III)hydroxides (Matthes, 1990). Strong correlation of uranium with most of the heavy metals in the sediments (except for Cr/Ni all heavy metals correlate with U on R >0.90; n: 8-12) suggest that unspecific co-precipitation dominates over selective adsorption according to valency and ion-size. Since seepage from tailing deposits usually contains high concentrations of dissolved Fe^{2+} and Mn^{2+}, which stay in solution in the reducing groundwater, a fairly high amount of both metals is available to remove uranium from the groundwater by precipitation. Extensive reddish and brownish iron crusts, often found where seepage enters the stream, are visible evidence for the process. However, precipitation preferably occurs in the interstitial of bottom sediments at the groundwater-stream interface, where the chemocline between reducing and oxidising conditions constitute an effective geochemical barrier for groundwater transported metals. Since precipitation happens rather fast, sediments not only act as a sink for contaminants but also prevent further fluvial downstream transport. Under the condition that groundwater instead of stream water in fact contaminates the bottom sediments a Kd of about 100 results. This is in range with those found in the floodplain system and suggests that redox-initiated precipitation also occur in floodplain soils. This seems likely since frequent fluctuations of the shallow groundwater table in the floodplain simultaneously also change the redox status of the sediments.

6. Conclusion

The results show that solute transfer of uranium from slimes dams is a major mechanism of contamination. In contrast to the particle-bound transport by erosion this leads to re-accumulations in the environment, which often exceed even uranium levels in the source of contamination. Precipitation processes in the stream, rather than adsorption on floodplain sediments determine the extent of diffuse stream contamination. Since the major immobilisation processes are highly depended on pH and Eh changes in stream water chemistry (as they are analysed in part III) are likely to affect the rate of downstream uranium-transport.

Acknowledgements

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