

Gold tailings as a source of water-borne uranium contamination of streams - The Koekemoerspruit[#] (South Africa) as a case study

Part III of III: Fluctuations of stream chemistry and their impacts on uranium mobility

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Abstract

Once dissolved uranium (U) from tailings deposits enters adjacent streams, subsequent downstream transport is affected by the rate at which U is immobilised in sediments, thereby lowering its concentration in stream water. For aqueous phases immobilisation includes adsorption onto sediments and suspended solids, as well as precipitation and co-precipitation as insoluble compounds, all mechanisms being largely controlled by pH and redox potential (Eh) of the stream water. Using real-time *in situ* measurements pronounced diurnal oscillations of both parameters were found at the site described here. The influence of the position of probes in detecting such short-term variations of stream-water quality are analysed by comparing in-house with in-stream measurements. Diurnal pH-oscillations are mainly caused by photosynthesis-based shifts of the calcium carbonate – carbon dioxide equilibrium in the stream that, in turn, is influenced by geological features of the catchment, biological activity as well as meteorological factors. These oscillations are likely to affect the mobility of dissolved U as well as the rate and distance of the downstream transport of U and other heavy metals significantly. Apart from this, event-related changes of stream chemistry, such as a sudden fall in pH in response to acid rain, were also observed. The dynamics and possible impacts on re-mobilisation of U from contaminated sediments back into the stream water are explored.

Keywords: diurnal fluctuations, pH, redox-potential, electrical conductivity, U, speciation, pH-Eh-stability diagram, mobility, immobilisation, re-mobilisation, acid rain, events, real-time measurements

Introduction

Water-borne stream contamination is mainly facilitated by the transport of U from adjacent tailings as an aqueous phase with a certain amount of U possibly transported in colloid form (particles 1 to 10 μm) (Whittow, 2000:97, Zänker et al., 2002). Being generally of low significance in carbonate-rich water where under normal pH conditions colloidal U-transport is largely prevented by complexation (Zänker et al., 2002), this paper on a dolomitic stream (where particular high carbonate concentrations are found) concentrates on mechanisms affecting the mobility of truly dissolved U.

Adsorption onto sediments or precipitation and co-precipitation as insoluble compounds can remove dissolved metals from the migrating water body. While this leads to the contamination of sediments, it reduces further water-borne distribution of the metals in the environment, at least for as long as the metals are retained in the sediment. Therefore, the higher the immobilisation rate, the lower the mobility of metals in aquatic environments. This also applies to streams. Here, however, the term immobilisation has to be understood in a hydrochemical rather than a mechanical sense, since not all solids in the fluvial system to which U might be attached, can be regarded as physically immobile. This is true

particularly for suspended solids and amorphous gels of oxyhydroxides, which may precipitate on top of stream-bed sediments. Both are easily moved down the stream channel by suspension in flowing water with oxyhydrates also forming uraniferous colloids of exceptional high mobility in freshwater systems under certain conditions (Zänker et al., 2002)

Speed and range of downstream transportation for dissolved metals is, on average, remarkably higher in solute form than as solids, since the latter tend to settle somewhere along the way. Moreover, dissolved metals display a significantly higher bioavailability and are more likely to pass through less sophisticated purification systems into drinking water supply schemes. In addition, the toxicity of metals for humans often increases with their solubility. Owing to the fast and far-reaching distribution by flowing water throughout the biosphere and their comparably high hazard-potential, the transport of dissolved metals in streams is of particular concern.

Solubility of metals depends to a large extent on their chemical speciation. In water of constant chemical composition speciation, in turn, is largely controlled by pH and redox-potential (Eh), as expressed in pH-Eh-stability diagrams (Pourbaix, 1985; Sigg and Stumm, 1991; Geipel et al., 1995; Wade et al., 2000).

In this study the temporal variation of these two 'master variables' in the Koekemoerspruit is investigated. This is of particular interest for assessing the mobility of U within the fluvial systems, since possible fluctuations of pH and Eh in streams may allow for U to change between dissolved and solid phases. The

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

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TABLE 1 Details of data logger and probes used				
Datalogger	Probe			
	Parameter	Brand, features	Measuring interval	Calibration method
DL2e "Delta T" (UK) outside stream with wired probes	EC	Kelvin, T-compensated 25°C	10 min	EC-field meter
	pH	WTW, T-compensated 25°C	10 min	pH-buffers, field meter
	Tw	pT 100	10 min	EC/pH-field meter
	Eh	Kelvin, T-compensated 25°C	10 min	Eh-standard, field meter

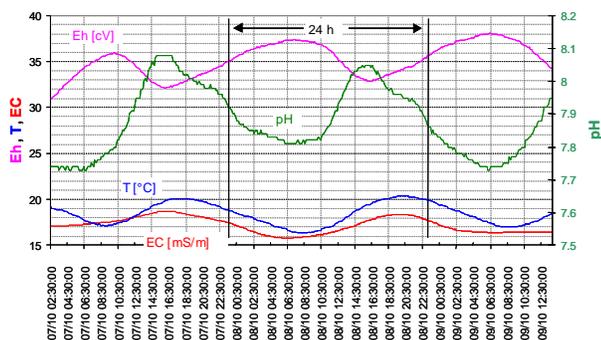


Figure 1
Diurnal oscillations of selected parameters in the Koekemoerspruit (observation period 7-9 October 1999)

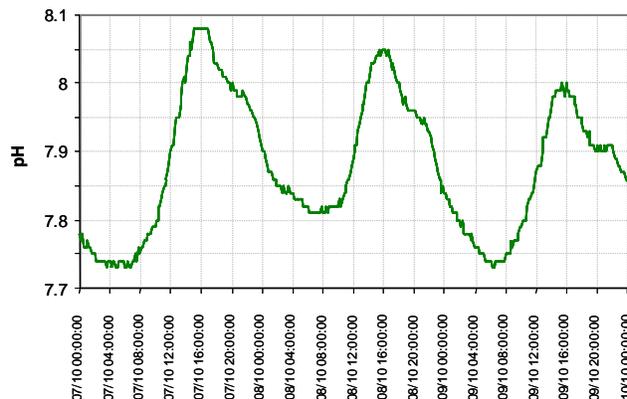


Figure 2
Diurnal fluctuations of the pH in the Koekemoerspruit (observation period: 07-10 October 1999)

emphasis is placed on the pH-value that largely controls the stream chemistry. Implications for the mobility of U in the fluvial system are discussed, including an analysis of causes and temporal changes of diurnal and event-related fluctuations of pH and related parameters such as redox-potential (Eh) and electrical conductivity (EC).

Study area

All measurements were taken in the Koekemoerspruit at station C2H139. The study area is described in Winde et al., 2004).

Methods

The set-up and structure of the automatic data-logging station employed for recording the real-time measurements are described in Winde et al., 2004. Details of brand, features and calibration method for each type of probe are given in Table 1.

An AgCl electrode-based probe was used to measure the redox-potential (Eh). To convert its readings into the hydrogen-based scale, 211 mV (for water with $T = 25^{\circ}\text{C}$) had to be subtracted. All probes were calibrated frequently against standard-solutions and laboratory-calibrated field meters respectively. The probes floated in the stream measuring about 100 mm below the water surface. Meteorological measurements were also taken in addition to the listed parameters. These include air temperature and relative humidity as well as rainfall intensity and volume.

Results and discussion

Temporal variations of stream chemistry

Fig. 1 shows selected parameters in the Koekemoerspruit over a 2 d period, displaying distinct diurnal oscillations.

Extent and dynamic of the oscillations illustrated above are discussed below with respect to possible causes and consequences for the aqueous downstream transport of dissolved U.

Variations of pH

The pH of the stream water starts to increase shortly after sunrise and reaches a maximum in the afternoon that is some 0.3 to 0.7 pH-units higher than the pre-sunrise level (Fig. 2). The pH then decreases towards a minimum at night-time which is frequently reached only shortly before the sun rises again.

According to Schwörbel (1987), pH-fluctuations in streams are mainly caused by photosynthesis of algae, phytoplankton and aquatic plants. These plants consume CO_2 dissolved in stream water for assimilation as soon as sunlight (UV radiation) is available. The carbon dioxide-calcium carbonate-equilibrium is shifted, resulting in increasing pH-values (Sigg and Stumm, 1991). Owing to the associated precipitation of calcium carbonate and the biological cause of the process it is termed 'biological decalcification' (Hellmann, 1999) and is to be distinguished from 'chemical decalcification' pertaining to karst areas, where changes in water temperature and/or atmospheric CO_2 pressure are primarily responsible for carbonate precipitation.

Owing to the dolomitic origin of the water in the Koekemoerspruit the stream contains relatively high concentrations of dissolved Ca^{2+} and HCO_3^+ . Precipitation of CaCO_3 quickly removes carbon dioxide and keeps associated pH fluctuations moderate (buffer capacity). In streams of non-dolomitic catchments with low buffer capacity, however, the amplitude of diurnal pH fluctuations can be much more pronounced, reaching up to two logarithmic units a day (Winde, 2002).

Apart from photosynthesis, concentration of dissolved CO₂ in stream water is also affected by the atmospheric CO₂ pressure and water temperature. While rising atmospheric pressure increases CO₂ levels, rising water temperature has the opposite effect. A change of water temperature from 10°C to 30°C, for example, causes a drop in dissolved CO₂ of some 50% (Sigg and Stumm, 1991). Since maxima of daily temperature cycles in streams commonly occur in the late afternoon, they are bound to amplify the 'biological' rise of the pH.

However, such amplification does not occur in the Koekemoerspruit, where a groundwater-pumping scheme disturbs the natural temperature regime. Owing to the geothermal gradient, groundwater pumped from >1 000 m below surface into the Koekemoerspruit has an elevated temperature of about 25°C (De Bruin, 2000). Depending on season and weather conditions, insolation, therefore, is frequently not sufficient to further heat the groundwater after being discharged into the stream. Instead of reflecting the insolation cycle during the day, the water temperature regime in the stream is dominated by cooling. With higher pumping rates at night (Winde and Van der Walt, 2004) reducing the cooling effect by increasing the water volume and a flow time of approximately one day between the point of discharge and the measuring station, temperature maxima in the Koekemoerspruit frequently occur only late at night (22:00 to 02:00) instead of in the afternoon like under normal conditions.

The effect of the delayed temperature maximum on the pH manifests itself as a secondary pH-maximum at night or, if less pronounced, as a 'shoulder' in the pH-graph, indicating an interruption of the pH-descent by staying constant for several hours (Fig. 3).

Fig. 3 also illustrates how the secondary pH-maxima coincide with nocturnal water temperature maxima. This is particular noticeable at days highlighted by arrows. In exceptional cases, when photosynthesis is markedly reduced (e.g. due to an overcast sky), the temperature-triggered pH-peak at night might even be higher than the one caused by photosynthesis during the day. In such cases the weak first maximum of the day forms a 'shoulder' on the left-hand side of the pH-curve. This phenomenon was observed just before thunderstorms when heavy clouds attenuated the insolation. The amplitudes of diurnal pH-fluctuations were also found to vary seasonally, reaching a maximum during spring, when day-night temperature differences are the highest and blooming of algae increases photosynthesis (Winde, 2003). Processes and factors controlling the diurnal dynamic of the pH are given in Fig. 4.

Variations of the redox potential (Eh)

The time series of the change in Eh show that it fluctuates inversely to the pH (Fig. 5).

Since the Eh indicates the concentration of free electrons in the system and the pH represents the concentration of H⁺ ions, a close relationship was expected, illustrating the inverse nature of the parameters. An analysis based on long-term time series, however, shows episodic drops of the Eh, for which no explanation could yet be found. Due to this only a very weak statistical long-term relationship between the two time series could be established. With amplitudes of 40 to 50mV per day, Eh fluctuations comprise about 11 to 15% of the daily maximum, usually occurring in oxidising ranges.

Variations of the electrical conductivity (EC)

Reducing the concentration of dissolved solids in the water by biologically triggered precipitation of CaCO₃ from the water col-

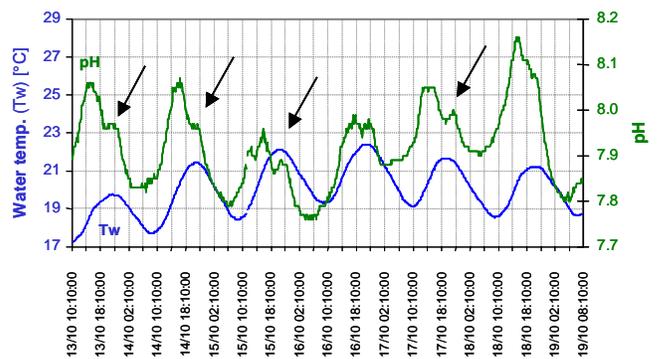


Figure 3
Second diurnal pH-maximum due to a late night maximum of the water temperature (observation period: 13-19 Oct 1999)

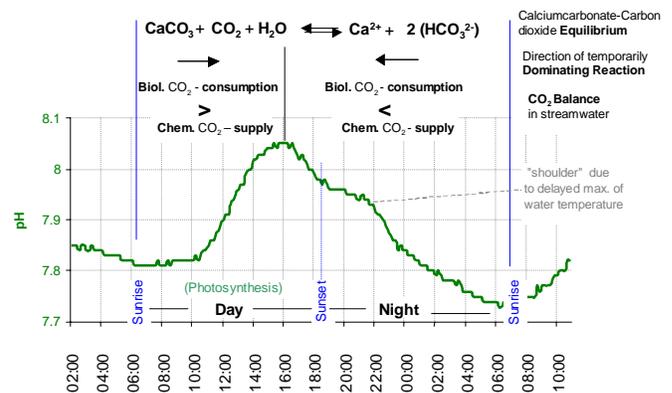


Figure 4
Processes controlling diurnal pH oscillations in the Koekemoerspruit (illustration based on an example of the pH-cycle observed on 8th October 1999)

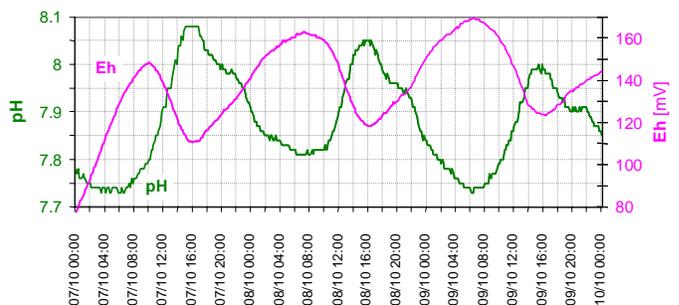


Figure 5
Diurnal oscillations of the redox-potential in the Koekemoerspruit in comparison to pH-oscillations (observation period: 07-10 October 1999)

umn, biological decalcification not only increases the pH of the stream, but simultaneously lowers the EC, resulting in an inverse relationship between pH and EC. While this was found in other mining-affected streams (Winde, 2002; 2003) it is not evident in the Koekemoerspruit. There, the daily maximum of the EC usually precedes the pH maximum by several hours, while the parameters do not oscillate inversely. No consistent statistically significant relationship could be established between the two variables by analysing long-term time series. However, a close link between EC and water temperature (Tw) was found. Despite a seemingly low similarity between both charts, EC and Tw are correlated with

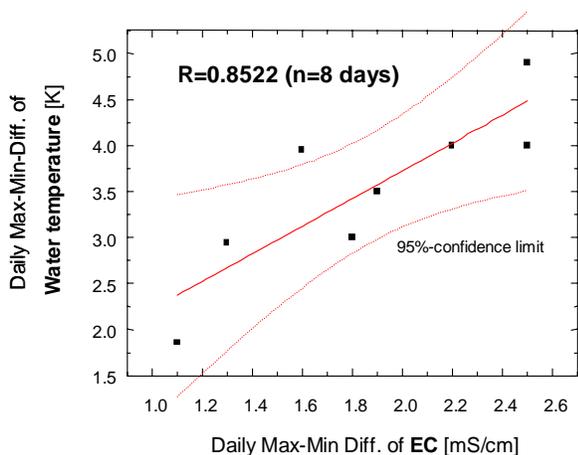


Figure 6

Linear regression between the amplitudes of daily fluctuations of EC and water temperature in the Koekemoerspruit (observation period: 06-13 November 1999)

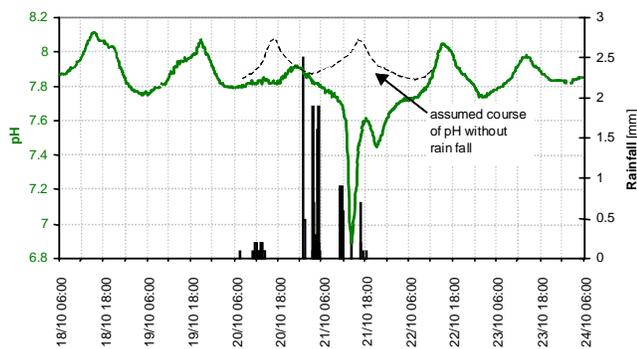


Figure 7

Response of the pH-value in the Koekemoerspruit to an acid rain event (observation period 18 -24 Oct 1999)

respect to the extent of their diurnal amplitudes. A comparison of the differences between the daily maxima and minima of both parameters reveals a significant linear correlation ($R = 0.85$) (Fig. 6).

The relationship found above is plausible, in light of the fact that the EC rises with temperature due to a higher mobility of the charged ions (WTW, 1993). However, the influence of temperature in all EC-probes was electronically compensated to a common reference value of 25°C. Therefore temperature fluctuations should not directly cause any EC variations. A possible explanation is the indirect effect of water temperature on the electrical conductivity by shifting temperature-dependent states of dissociation-equilibria (WTW, 1993).

Impacts of rain events on the hydrochemistry of the stream

Rain-triggered pH changes occur less frequent than diurnal changes but are often more pronounced and last longer. Figure 7 shows an example of the effects of a rainfall event on the pH in the Koekemoerspruit.

The pH in the stream drops by about one unit to a value of 6.8 within a few hours of rainfall due to acidic rainwater (a minimum pH of 3.7 was measured). Taking the diurnal fluctuation of the pH into account, the drop actually comprises >1.2 pH units, since the

decrease coincides with the daily pH maximum (dashed line in Fig. 7). This means that, in cases where rainstorms occur during the daily pH minimum, an even bigger pH drop is likely. Therefore, the hydrochemical impact of rain events on streams not only depends on the pH of the rainwater and the rain intensity but also on the point in time the event takes place.

Since low pH values in general favour dissolution of U from sediment, pulses of dissolved U in the stream shortly after acid rain events may occur. This is of particular concern in poorly buffered streams.

In the analysed rain event the resulting minimum of the EC occurs about 2 h later than that of the pH. This is somewhat surprising in so far as both parameters reflect the impact of rainwater and it was therefore assumed that they would react simultaneously. After the rain stopped, the EC stayed below normal for another 37 h, suggesting that (comparably clean) surface runoff still diluted the stream. An increased inflow of alluvial groundwater into the river, as another possible explanation for the long-lasting dilution effect can be excluded, since the alluvial groundwater actually shows a higher EC than the stream. Compared to the 37 h of the EC the pH 'recovered' rather quickly, showing normal oscillations again only 12 h after the rain had stopped.

In-house vs. instream measurements

Parallel to the measurements presented here, EC and water temperature of the Koekemoerspruit were recorded in 30 min intervals by the DWAF, using an electronic data-logger (DWAF, 1999). In contrast to the probes described in this paper, which were floating on the stream surface outside the gauging hut, probes used by the DWAF were placed inside the gauging well of station C2H139. Comparing time series of EC and water temperature measured during a six-day period in October 1999 by both sets of probes, distinct differences are discernible (Fig. 8).

While measuring approximately the same value for EC and water temperature, Fig. 8 clearly indicates that the probes inside the gauging well do not reflect diurnal fluctuations or other short-term variations of both parameters that were recorded in the stream itself. The most likely reason for this is a rather low rate of physical exchange of water between the stream channel and the gauging well, which are interconnected by a ca. 2 cm-wide pipe. While the pipe suffices for transmitting stream level changes to the connected gauging well, it apparently does not facilitate the necessary rate of through-flow of stream water through the well to allow for the detection of short-term changes of stream water quality. It seems that water in the gauging well is rather stagnant most of the time (particularly when no stream level changes take place), and hardly affected by any short-term change of water quality in the stream channel. With the probes being frequently re-calibrated and well maintained by the DWAF, it is assumed that a decrease of their sensitivity can be excluded as possible reason for the less dynamic records observed.

It needs to be considered, however, that larger time intervals between measurements also tend to decrease the recorded amplitude of short-term variations of stream water quality, simply through the increased likelihood of missing out on extreme values that might occur between two measurements. Since calculated hourly means of the 10 min instream data still reflect diurnal and other short-term fluctuations of the water temperature and the EC, it is unlikely that the slightly longer time interval used by the DWAF is responsible for the distinct differences of the chart dynamics.

Implications of the fluctuating stream chemistry for mobility and transport-rates of U in streams

As found by Hellmann (1999) for the River Rhine in Germany, biological decalcification often reduces the concentration of dissolved heavy metals in stream water by precipitating them along with CaCO_3 (calcite). The calcite was often found to precipitate on suspended solids as crusts ("Aufwuchs") also raising their grain size and modifying transport behaviour. A high correlation ($R = 0.839$; $n = 6$) between the CaCO_3 content and the U concentration in bottom sediments indicates that this process also takes place in the Koekemoerspruit (Winde et al., 2004). It is therefore to be expected that diurnal variations of decalcification intensity are mirrored by daily cycles of U levels in stream water.

Since amplitudes of daily oscillations vary throughout the year, seasonal effects on the metal concentration in streams also need to be taken into account. This applies in particular to monitoring programmes, which will not obtain representative data unless sampling routines are adapted to these temporal patterns. With respect to the latter, the location of probes for water quality parameters also needs to be reconsidered, ensuring sufficient contact with flowing stream water to allow detection of short-term variations in stream water quality. Indicating not only diurnal cycles of water quality parameters but also the effects of events such as spills of wastewater from various sources into the stream, acid rainfall etc., the detection and interpretation of short-term variations in stream water quality is indispensable for a comprehensive monitoring programme. As a practical application for understanding the dynamics of metal concentration in streams, a model could be developed to advise downstream users when not to extract water to avoid obtaining dissolved metals at peak occurrences. Apart from co-precipitating along with calcite, metals can also be immobilised by varying pH and Eh conditions, which affect the speciation of dissolved metals. For dolomitic water an example of the influence of both parameters on the speciation of U is shown in Fig. 9.

The pH-Eh-stability diagram was generated using the thermodynamic speciation model (JESS), with the European Chemical database, and is adapted from Wade et al. (2000). It suggests that the observed diurnal fluctuations of pH and Eh are not likely to have profound effects on the speciation of U in the Koekemoerspruit. However, in terms of U mobility, the diagram suggests that a pH drop of below 6 (while maintaining normal oxidising conditions) may allow U to stay in solution instead of being immobilised by co-precipitation with calcite.

As mentioned above, effects of Eh changes on the U mobility in the stream within the oxidising region are rather small, compared to pH effects. Apart from controlling calcium carbonate precipitation, pH also affects the precipitation of iron and manganese oxides/hydroxides as a major mechanism for immobilising U in the Koekemoerspruit (Winde et al., 2004). Its profound impact on this type of immobilisation is illustrated by the fact that the rate of iron(III)hydroxide precipitation increases over hundredfold if the pH [and thus the (OH^-) concentration] rises by one logarithmic unit (Sigg and Stumm, 1991). In addition to this, the precipitation of dissolved Fe(II) as $\text{Fe}(\text{OH})_3$ - without bacteria - is only possible in a neutral-alkaline environment with $\text{pH} > 7$. The precipitation of manganese as hydrous oxide or oxide (MnO_2), which also removes dissolved U from the water column, requires even higher pH values (> 8.5) (Jenne, 1995; Luther, 1995).

In addition to the co-precipitation of U with the aforementioned compounds, the subsequent adsorption onto precipitated gels is also controlled by pH (Jenne, 1995). The surface-charge of hydrous iron oxides, for example, only turns negative (thereby

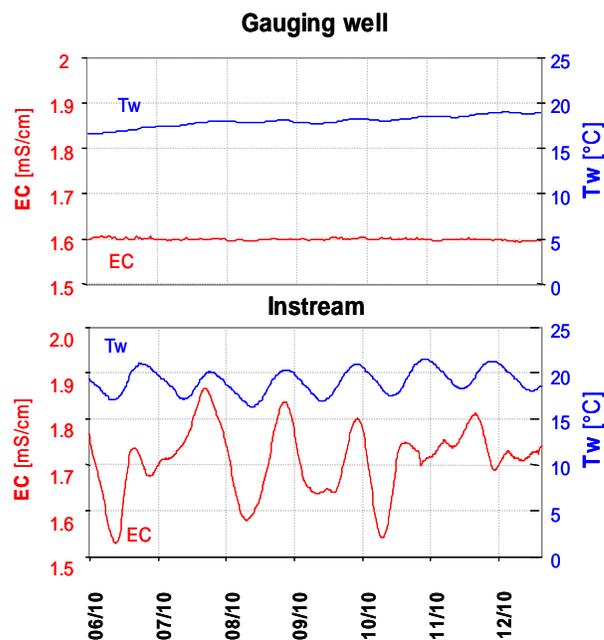


Figure 8

Time series of water temperature and EC for the period 06-12 Oct 1999 as recorded by sensors placed inside of the gauging well of a gauging hut (upper diagram, data recorded at 30 min intervals; DWAF, 1999) and sensors placed outside the gauging hut directly in the running streamwater as used in this study (lower diagram, data recorded at 10 min intervals)

being receptive for positively charged U species and free cations) when the pH rises above 8. As long as the pH is lower, no adsorption of U compounds onto the precipitated gels, which due to their large reactive surface are regarded as important catchers for dissolved U (Wade et al., 2000), can take place.

Comparing these thresholds with the diurnal pH fluctuations observed in the Koekemoerspruit, a number of the immobilisation processes discussed are only possible during certain times of the day. It seems therefore that the mobility of U and its concentration in stream water are generally higher during the night. In daytime biological decalcification removes dissolved U directly from the stream by co-precipitation and simultaneously causes the pH to rise. Reaching pH values of 8.0 and higher in the course of the day, allows for hydrous Fe/Mn oxides to precipitate and to additionally immobilise U by co-precipitation and subsequent adsorption onto the large surfaces of freshly precipitated gels.

While precipitation happens rather quickly (within minutes) dissolution of solid compounds is, in general, a much slower process (Mattheß, 1990). It is to be expected, therefore, that fluctuating pH values affect the rate of U immobilisation in the stream rather than actually causing the release of U from sediments (re-mobilisation). This might be different in cases where the pH drops are triggered by acid rain, which then last much longer and are more pronounced. Streams in non-dolomitic catchments are particularly prone to heavy metal re-mobilisation from sediments due to such rain events. Furthermore, in some headwater regions of streams in the Witwatersrand (South Africa), acidic seepage from adjacent slimes dams constitutes a remarkably high proportion of the total streamflow (Winde and De Villiers, 2002b). With decreasing rainfall and dilution during the dry winter months, the upper reaches of some of those streams consist almost entirely of acid mine drainage. Apart from the metal input that is associated with

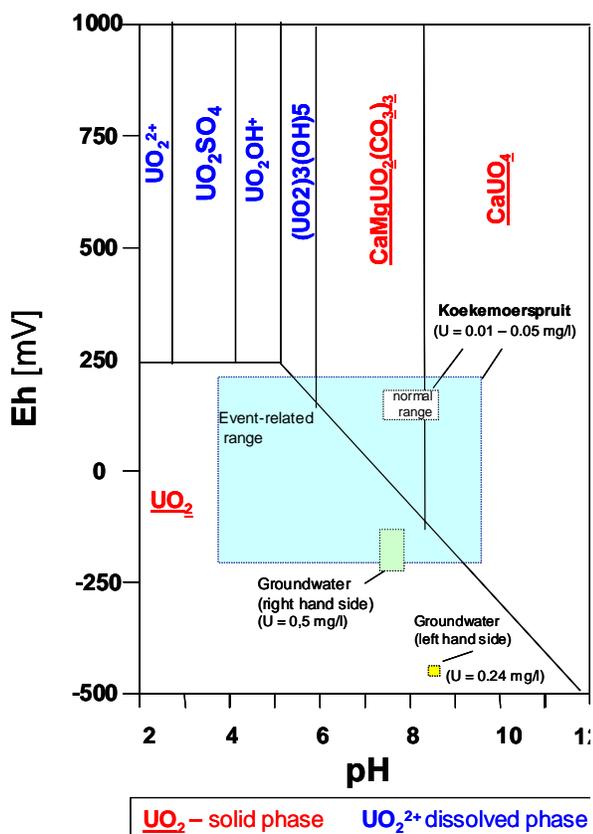


Figure 9

A pH-Eh-stability diagram for 1 μM U in dolomitic water in comparison with the range of pH and Eh values observed in stream and groundwater at the study site

the seepage inflow, this simultaneously leads to long-lasting drops of the pH, which favour the release of U from stream sediments during the dry season.

Synoptic summary of dynamics and mechanisms of water-borne stream contamination with U from adjacent tailings deposits (incl. Part I and II: Winde et al., 2004; Winde and Van der Walt, 2004)

Chemical analyses of water and sediment samples from the Koekemoerspruit have established the significance of gold and U slimes dams as sources of water-borne stream contamination. Dissolved U and other heavy metals move along with seepage from tailings deposits into groundwater, which finally seeps into the Koekemoerspruit. A rapid increase of the U concentration in tailings, resulting from the abandonment of U production by many mines, has significantly elevated the potential of slimes dams for U pollution of adjacent streams.

En route to the stream, U passes through several sediment-water systems where different mechanisms partly remove the dissolved metal from the water column by turning it into solid phases. Within the stream, precipitation of calcite and iron-manganese hydroxides was identified as the most important mechanisms for immobilising U. The precipitation of iron manganese hydroxides occurs in particular within the bottom sediments of the stream channel. As an interface between reducing groundwater and well-oxygenated stream water, the interstices act as a geochemical barrier for U and other dissolved heavy metals. Protected from the

eroding power of flowing water, the precipitated gels can accumulate in the sediment pores and crystallise over time into genuine solids constituents of the sediment.

While retaining U in the sediments helps to reduce water-borne stream contamination further downstream, it simultaneously creates off-site accumulations of the radionuclide, which may act as secondary sources of contamination, as was found for sulphate crusts on floodplain sediments.

Since alluvial groundwater is the main source of U contamination in the Koekemoerspruit, the actual stream pollution depends not only on the concentration of U in the groundwater but also on the volumes (rate) at which polluted groundwater infiltrates the stream. This, in turn, is largely controlled by man-made fluctuations of gauging heights in the stream channel, resulting from a pumping scheme. By causing even higher fluctuations of the groundwater level in the adjacent floodplain, this leads to highly dynamic stream - groundwater interactions, including daily reversals of the direction of flow between the two water bodies. At certain times of the year, this allows contaminated groundwater to seep into the stream only at night. Since current monitoring programmes do not detect this, sampling and measuring protocols should be adjusted to these variations.

Once U has entered the stream, the rate of downstream transport mainly depends on its speciation, which determines whether the metal stays in solution or becomes immobilised as solid phase. This, in turn, is largely controlled by pH and Eh of the stream water, both showing distinct diurnal oscillations; while dolomitic stream water in the Koekemoerspruit constitutes a well-buffered (alkaline) system, which only allows the pH to oscillate by about half a unit per day. In non-dolomitic streams pH fluctuations of up to two units per day were found. This constitutes a significant change of chemical conditions that determine U transport in streams. The rate of precipitation of iron hydroxides - which removes U from the water column - is about 10 000 times higher during the pH-maximum in the late afternoon than in the early morning or during the night.

In the Koekemoerspruit, daily fluctuations of the hydraulic groundwater input and oscillations of stream chemistry are superimposed. This largely prevents dissolved U from being removed by co-precipitation. Since groundwater exfiltration into the stream occurs preferentially at night, when no photosynthesis takes place, it mixes with the stream water having a low oxygen concentration. With concurrent low pH values during this time, a comparatively poor immobilisation rate is to be expected. Furthermore, biological de-calcification and the associated U immobilisation only occur during daytime. Therefore, in U contaminated streams it is to be expected that higher concentrations of dissolved U are found at night. In general, Eh fluctuations are likely to have a lesser effect on U speciation than those of pH.

It can be concluded that U transport in streams is determined by the net effect of two processes: the hydraulic dynamics of stream-groundwater interaction (often modified by mining) and diurnal oscillations of stream chemistry, mainly of natural origin. In addition, event-triggered changes of water chemistry occur. In this regard acid rain is of particular concern since it lowers the pH in the stream and favours re-mobilisation and high mobility of U. Apart from the pH of the rainwater and rain intensity, the point in time at which the rain event takes place also determines the impact on the stream. Associated consequences for U mobility are of particular concern in streams with low buffer capacities, where rain-triggered drops of pH are more pronounced and last longer. However, the main effect of diurnal and event-related pH fluctuations seems to be to prevent dissolved U from being immobilised rather than the dissolution of U from sediments.

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