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URANIUM CONTAMINATION OF FLUVIAL SYSTEMS - MECHANISMS AND PROCESSES

PART III: DIURNALAND EVENT-RELATED FLUCTUATIONS OF STREAM CHEMISTRY - PITFALLS FROM MINING AFFECTED STREAMS IN SOUTH AFRICA, GERMANYAND AUSTRALIA

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ABSTRACT: Once dissolved uranium from tailings deposits has entered the stream downstream-transport depends not only on the flow conditions in the streams but also on the rate of immobilisation. The latter comprises all hydrochemical processes in which dissolved uranium turns into solid phases, which can accumulate in the stream channel. It includes adsorption onto sediments and suspended solids, as well as precipitation or co-precipitation as insoluble compounds. While immobilisation removes dissolved uranium from the water column, it simultaneously leads to the contamination of the sediments in which the radionuclide is retained. The rate of immobilisation of metals in aquatic environments is strongly controlled by their speciation. This in turn largely depends on the pH and redox-potential of the system. Independently from the climatic region in all studied streams, pronounced diurnal fluctuations of both parameters were found. However, the amplitude of the daily oscillation and the covered range of the pH differs remarkably. While photosynthesis based shifts of the calciumcarbonate-carbondioxide-equilibrium are the main cause of the fluctuations, also impacts of the geology, the season and meteorological parameters were found. With changes of the pH of up to two logarithmic units per day, these processes are likely to have profound effects on the rate of immobilisation and thus the downstream transport of dissolved uranium. Interactions and dependencies between the fluctuations of various parameters are analysed and their implications for the uranium behaviour in the system is discussed. Apart from diurnal fluctuations, also event-related changes of the stream chemistry, like sudden drops of the pH in response to acid rain fall, were observed. Their impacts of the remobilization of uranium and other heavy metals from sediments, which might resulting in short duration peaks of pollution, are also analysed.

RESUMEN: Una vez que el uranio disuelto procedente de escombreras ha llegado al río, el transporte aguas abajo depende no sólo de las condiciones del flujo en los ríos sino también de la tasa de inmovilización. Esta *última comprende todos los procesos hidroquímicos por los que el uranio disuelto regresa a fases sólidas, que pueden acumularse en el cauce fluvial. Esto incluye la absorción en sedimentos y sólidos en suspensión, así como la precipitación o co-precipitación como compuestos insolubles. Mientras que la inmovilización retira uranio disuelto del agua, a la vez conduce a la contaminación de los sedimentos en los que el radionucleido es retenido. La tasa de inmovilización de metales en ambiente acuático está fuertemente controlada por su especiación. Ello a su vez depende del pH y potencial reductor del sistema. Con independencia del ambiente climático, se registraron fuertes fluctuaciones diarias de ambos parám,etros en todos los ríos estudiados. Sin embargo, la amplitud de la oscilación diaria y el rango del pH difieren notablemente. Aunque los cambios en el equilibrio carbonato cálcico-dióxido de carbono basados en la fotosíntesis son la principal causa de las fluctuaciones, también influyen la geología, la estación del año y diferentes parámetros meteorológicos. Con cambios de pH de hasta dos unidades logarítmicas por día, estos procesos deben tener profundos efectos en la tasa de inmovilización y en el transporte de uranio disuelto. Se analizan las interacciones y dependencias entre las fluctuaciones de varios parámetros y se discuten las implicaciones para el comportamiento del uranio dentro del sistema. Aparte de las fluctuaciones diarias, también se han observado cambios en la química del río durante eventos concretos, como súbitas caídas del pH en respuesta a la lluvia ácida. También se analizan sus efectos en la removilización de uranio y otros metales pesados, que podrían dar lugar a picos contaminantes de corta duración.*

Key-words: Uranium, Tailings, Contamination, Heavy metals, Fluvial system, South Africa.

Palabras clave: Uranio, Escombreras, Contaminación, Metales pesados, Sistema fluvial, Sudáfrica.

1. Introduction

Uranium and other heavy metals from tailings deposits only migrate along the groundwater-path as long as they are in a solute form. However, adsorption onto sediments or precipitation/co-precipitation as insoluble compounds, can extract dissolved metals from the migrating water column (immobilisation processes). While this leads to the contamination of sediments (e.g. floodplain soils) it simultaneously prevents further transport into the environment. Thus, the higher the rate of immobilisation for a specific metal, the lower its mobility. The same concepts apply to the fluvial transport in stream channels. There, however, the term “immobilisation” is used in a hydrochemical rather than a mechanical sense, since not all solids in the fluvial system to which metals/uranium get attached, can be regarded as physically immobile. This in particular is true for precipitating gels and suspended solids. However, speed and range of downstream transport for dissolved metals in average is much higher than for solids, since the latter tend to settle out of the water-column along the way or are not moving at all until flood-events occur (e.g. coarser bottom sediment, bank substrate). In addition to this, solute metals are much more bio-available than solid forms and thus of greater risks for downstream users.

Due to the fast distribution within the environment and the higher hazard potential, the solute phase of uranium and other heavy metals is of particular concern.

The solubility and the ratio between dissolved and solid phases of metals strongly depend on the speciation (the chemical form) in which the metals appear. Given a solution of constant chemical composition speciation almost exclusively depends on the pH-value and the redox-potential (Eh) of the aquatic environment (pH-Eh-stability diagrams). In order to check for critical changes of chemical conditions in the stream, which may allow for transitions between solute and solid phases and thus influence the fluvial mobility of uranium, both parameters were recorded in high time-resolution. Using datalogger-controlled probes in addition to pH and Eh, also water-temperature and electric conductivity (EC) was measured in ten-minute intervals over periods of up to two years.

All studied streams are affected by nearby uranium mines, which are either active ore closed. Each of the streams represents specific climatic conditions that not only impact on the fluvial dynamic but were also thought to be influential in terms of hydrochemical processes in the stream. Since not all results are available yet a finale comment on the latter can not be made. Although results from Germany and Australia are presented the emphasis is still placed on the Koekemoer Spruit, as it was in part I and II.

Apart from analysing diurnal and event-related fluctuations of the relevant hydrochemical parameters, also implications for the mobility of uranium in the fluvial system are discussed

2. Study sites

Real time in situ measurements of hydrochemical parameters were carried out in all three streams mentioned. In the following, a brief description of the sites is given. The numbers in brackets behind the country indicate longitude, latitude and altitude of the datalogger station used)

Lerchenbach (Thuringia, Germany: 12°12’10” East; 56°30’16” North; 272m).

The Lerchenbach is a small perennial stream, which is affected by seepage from tailing ponds (IAA Truenzig and IAA Culmitzsch) of a closed uranium mill of the former Wismut Company (Figure 1).

The stream shows a natural discharge at the point of impact of about 0.11m^3/s (annual average) yielded from a gently sloped catchment of some 15km^2 with dominating agricultural use and shales and sandstone in the geological underground. Together with purified wastewater discharges from the tailing ponds the mean annual flowrate is about 0.46m^3/s. The flow distance between point of impact and discharge into the Weisse Elster is 10km. With 600mm of mean annual precipitation (MAP) with a maximum during the summer month (June-September) and a mean annual runoff (MAR) of about 200mm (33% of MAP) the climate is humid. The seepage from the tailings ponds migrates across the alluvial aquifer of the associated floodplain (“Culmitzschaue”) into the stream, preferably moving along a small band of highly permeable “Culmitzsch”

Figure 1. Location of the study site "Lerchenbach" in Germany.

sandstone. The 4 ponds contain about 108 million tonnes of water-covered tailings from sulphuric acid and (to a less extent) soda-alkaline leaching processes with an average uranium concentration of 60-140ppm. The tailings are filled in former open pits reaching a thickness between 30m and 72m. With the covering water table located more than 70m above stream level and a minimal distance between the ponds and the stream of 100m, steep hydraulic gradients result, driving seepage forcibly towards the stream.

Koekemoer Spruit (North-West Province, South Africa: 27°02'40" East; 26°55'00" South; 1290m).

The Koekemoer Spruit is a small non-perennial stream, which is affected by seepage from tailings deposits of an active gold-and uranium mine (Buffelsfontein), which ceased uranium production in the 1980s. In addition to this, also seepage from an evaporation dam on the left-hand side seeps into the stream (Figure 2).

Figure 2. Location of the study site "Koekemoer Spruit" in South Africa.

Due to a pumping scheme, which prevents an adjacent goldmine from being flooded, a perennial flow of about 0.4m^3/s in the lower 14km of the stream is sustained by dolomitic groundwater. The flow distance between the point of impact and discharge into the Vaal River is some 5km. The almost even catchment (at the point of impact) is about 815km^2 in size, sparsely covered with grass and bushy vegetation mainly used for cattle grazing. While the geological underground overwhelmingly consists of shales and quartzite, the lower part is dominated by dolomite with developed karstic features, also underlying the tailings deposits and the evaporation dam. With less than 2% mean annual runoff from about 600mm/a precipitation (which mainly falls during summer rain storms from November to March, while winters are sunny and dry) and a potential evaporation of some 1700mm/a, the area is classified as semiarid. The tailings are deposited as "slimes dams" which consist of fine-grained material from which the surplus water –used to transport the slurry from the metallurgical plant- evaporates during the day. Whereas all slimes from which uranium was leached by sulphuric acid only contain 10-15ppm U$_{nat}$ the younger slimes, those deposited after uranium-production was ceased, display concentrations of some 130ppm. With heights of 10-50m above ground and a minimum distance to the stream of 300m, a comparably steep hydraulic gradient between tailings and stream results, which forces uranium-contaminated seepage to flow across the shallow floodplain-aquifer into the stream.

Magela Creek (Northern Territory, Australia: 132°55'45" East; 12°40'28" South; 12m).

The Magela Creek is a tropical stream in the Kakadu National Park, which -together with the associated floodplain- is affected by the active Ranger Uranium Mine (near Jabiru). Thirty kilometres further downstream, the Magela creek also passes the Jabiluka uranium-mining site that has not been brought into production yet (Figure 3).

The stream shows an extreme discharge-variability between the wet season (November to April: 100-1000m^3/s) (Le Gras, 2001 pers. communication) and the "Dry" (May-October) where in October often only water-holes ("billabongs") in the otherwise dry stream channel remain. The catchment area at the point of impact is about 100km^2 (estim.), mainly covered by wetlands. Granites and gneiss from the basement partly cov-

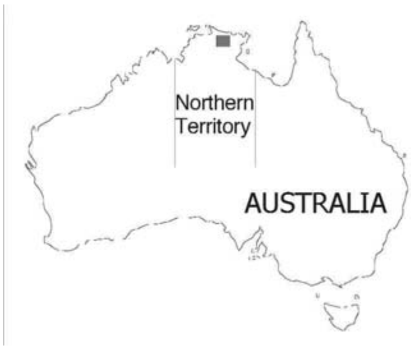

Figure 3. Location of the study site "Magela Creek" in Australia.

ered with non-carbonate sedimentary rocks, dominate the geology. With monsoonial rainfall of 1700mm (mainly during November to March) and extreme high evaporation rates during the dry season the stream reflects a marked tropical climate. The open pit mine produces high-grade ore with uranium concentration between 2000ppm and 4000ppm. The water saturated tailings dam contains about 25 million tons of sulphuric leached tailings with an average Unat-concentration of 200-400ppm. The tailings cover an area of about 1.5km^2, 2500m distant from the Magela.

3. Experimental

The measurements at all sites were taken by electronically probes, which were controlled by a computerised data logger. The types of the data-loggers and the probes differed for each study site.

At Lerchenbach a data logger from Delta T (DL-2e)(UK) powered by a heavy duty 12V battery was placed outside the stream with the probes in the stream connected via wires. For measuring electric conductivity (EC) electronically probes by Kelvin (Germany) were used compensating all measured data to a reference temperature of 25°C, repeatedly calibrated against a solution-calibrated field meter (WTW pH95, Germany). The pH-value was recorded by a WTW-probe, repeatedly calibrated against buffer solution and a buffer-calibrated field meter (WTW, pH95 Germany). The pH-measurements also were temperature-compensated to the reference-temperature of 25°C. A pT-100 probe, calibrated against the stated field-meter was used to measure water-temperature. After starting the measurements with 5min time interval the latter later was extended to 10min. covering a period of up to two years. The probes were placed about 5cm above ground, ensuring that they were also submerged during low-flow conditions.

Apart from a few minor modifications, the same instruments and set up were used at the Koekemoer Spruit. In addition to the said parameters, an AgCl-electrode based probe from Kelvin (Germany) also measured the redox-potential (Eh). The probe was frequently calibrated against a solution and field meters from WTW/testo. To convert the measured data into hydrogen-based scales (Eh) 211mV have to be subtracted (T=25°C). For measuring pH a temperature compensated Kelvin–probe was used, repeatedly calibrated against buffer-solutions and field meters (WTW). After about 1 month of permanent use increasing deviations from field meter readings and the given values for the buffer solution indicated that both probes could no longer be used. The probes were floating on the stream measuring in a depth of about 10cm beneath the water-surface. All data were recorded in ten-minute intervals for a maximal period of 2 years.

The data from the Magela Creek were obtained by a compact, submergible data-logger (“Hydrolab”, UK) which is battery-powered and includes probes for all stated parameters, including dissolved oxygen. The device was attached to a pontoon floating in the streamline of the Magela and the probes measuring in about 10cm below the water surface. All temperature depended parameters (pH, EC, Eh) were electronically compensated to the reference temperature of 25°C. The probes were calibrated against buffer solution. While data during the short-term campaign in April 2001 were recorded in ten-minute-intervals the 1-year measurement near Jabiluka is based on 30min-intervals.

In addition to said parameters at the Lerchenbach and the Koekemoer Spruit, also electronically meteorological measurements were taken. This includes temperature and relative humidity of the air as well as rainfall-intensity and -volume.

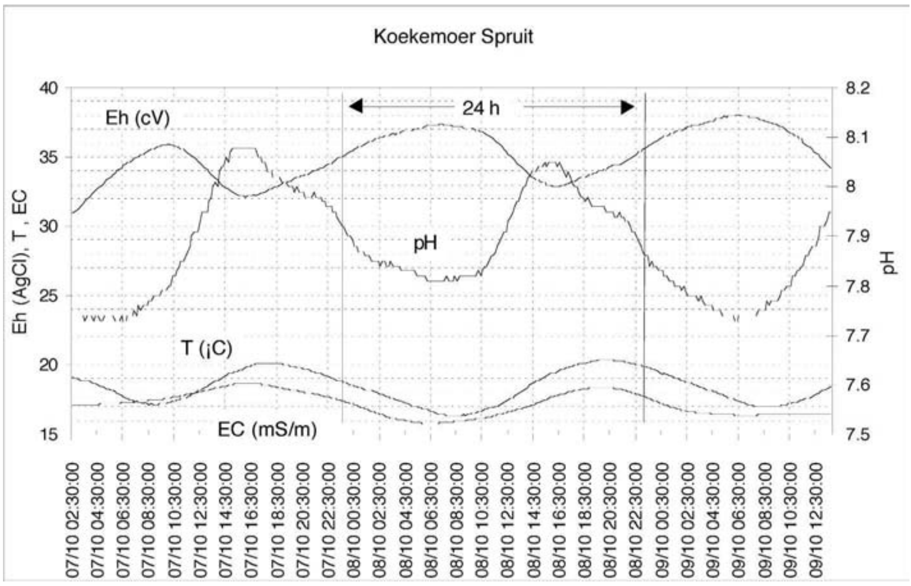

Figure 4. pH, Eh, Tw and EC in the Koekemoer Spruit over a 2-day period (7.-9.10.1999).

4. Results and discussion

4.1. Diurnal fluctuations of streamwater chemistry during dry weather

As figure 4 shows, during dry weather all recorded parameters in the Koekemoer Spruit show distinct diurnal fluctuations. Similar patterns were also found in the Lerchenbach (Germany) and the Magela Creek (Australia).

In the following the fluctuations of the pH are analysed with respect to their causes, interactions with other parameters including Eh, and the implications for the solute transport of uranium.

4.1.1. pH-fluctuations

a) Regional and seasonal variability of the amplitude

Koekemoer Spruit (South Africa)

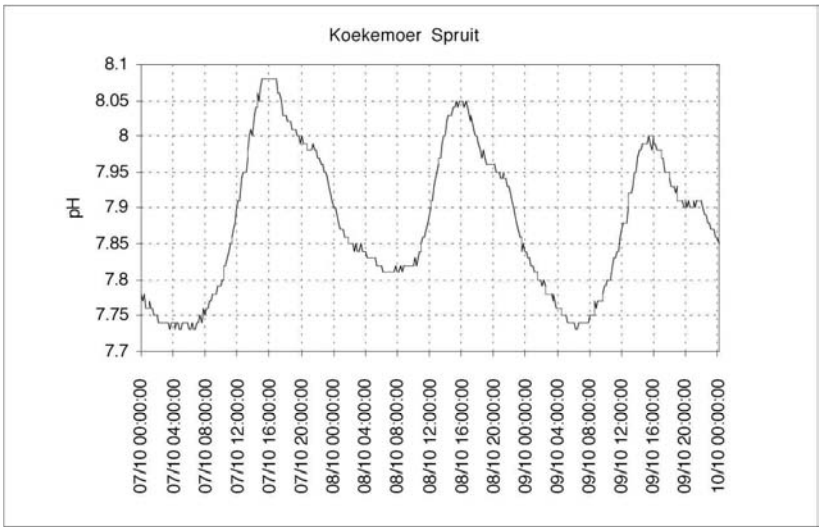

Figure 5. pH of the Koekemoerspruit during a dry weather period in October 1999.

As displayed in Figure 5 the pH of the stream shows distinct daily variations with the minimum usually occurring round about 6 a.m. (+/- 2h). During the day the pH than rises for up to half a unit to a maximum of 8.0 to 8.2. This maximum pH usually is reached in the late afternoon (16:00). In night time the pH decreases again approaching the stated minimum in the early mornings.

Due to alterations of the pH–probe over time only data for a period of 3 month could be used. Therefore no statements regarding the annual cycle of pH-fluctuations can be made.

Lerchenbach (Germany)

Figure 6 displays pH-fluctuations in the Lerchenbach recorded in April 1997. Starting from a daily minimum of pH 7.0 at about 6:00 the pH continuously rises during the day to a maximum of pH 9.0 at about 16:00. Comprising two units the pH-fluctuations represent a diurnal change of H^+-concentration by a 100 times.

While the diurnal amplitude is 4 times higher than in the Koekemoer Spruit the different time interval of measuring has to be taken into account as well. As Figure 7 shows a significant reduction of the daily amplitude occurred after the time interval between two measurements was extended from 5min to 10min. Although it can not be excluded that other factors were causing this drop in amplitude, it points to a general tendency. The longer the time between two measurements, the higher the likelihood to miss occurring extremes. This also is reflected by statistics with differing time-intervals as smallest units. While monthly statistics on basis of 10min data showed a minimum-maximum-difference of the pH of about 29% (of the recorded maximum), the same difference on basis

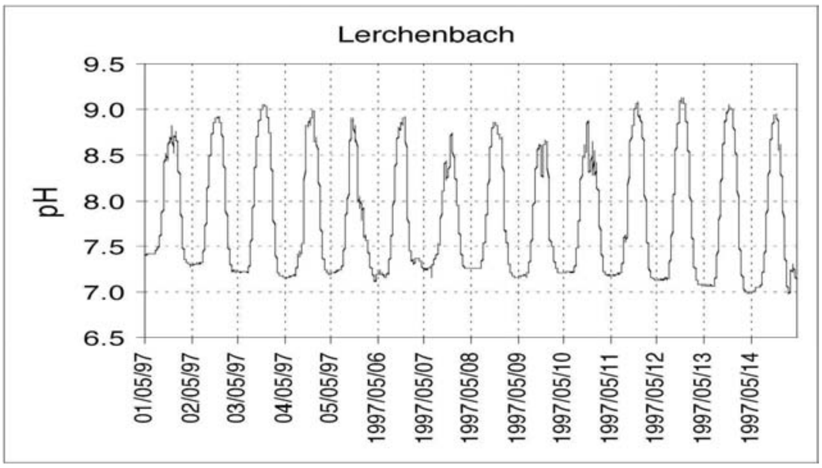

Figure 6. pH-fluctuations in the Lerchenbach (April 1997, 3 days, 5-min interval).

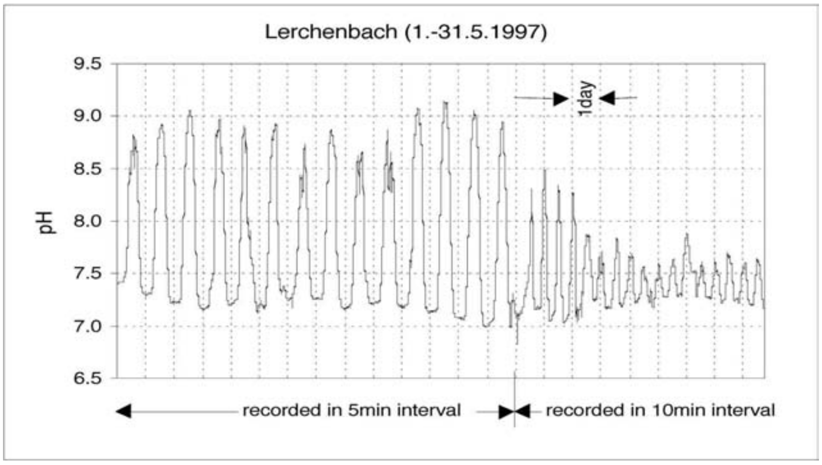

Figure 7. pH-chart during change between 5'and 10'interval.

of hourly averages (consisting of condensed 10min data) only displayed a 14%-difference, which is further reduced to 4% when daily averages were used.

However, long-term analyse yields that the amplitude of the diurnal pH-fluctuations varies throughout the year (Figure 8).

It clearly shows a maximum of daily fluctuations in spring of 2 units per day dropping down to about 0.5 units a day in summer and winter. Possible reasons for the seasonal behaviour of the daily pH-amplitude are discussed in connection with the analyses of causes for the observed diurnal pH-cycle.

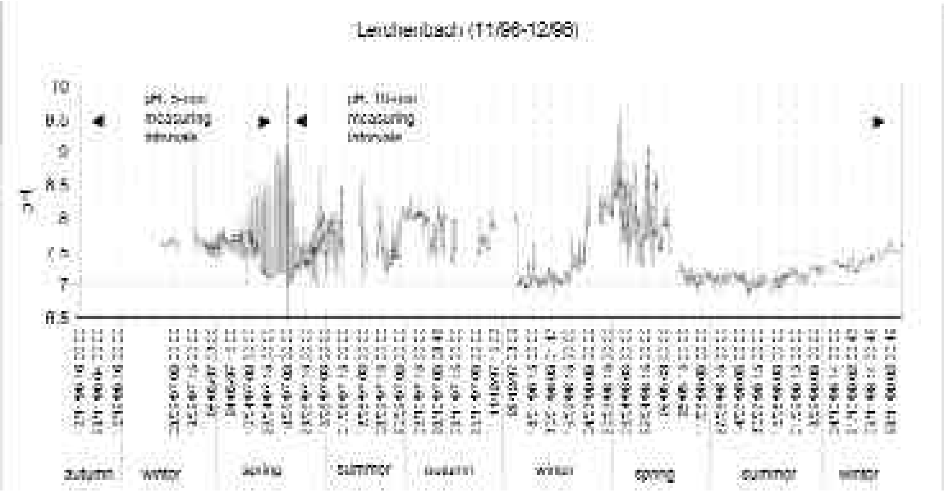

Figure 8. Seasonal fluctuations of the pH in the Lerchenbach (1997–1998).

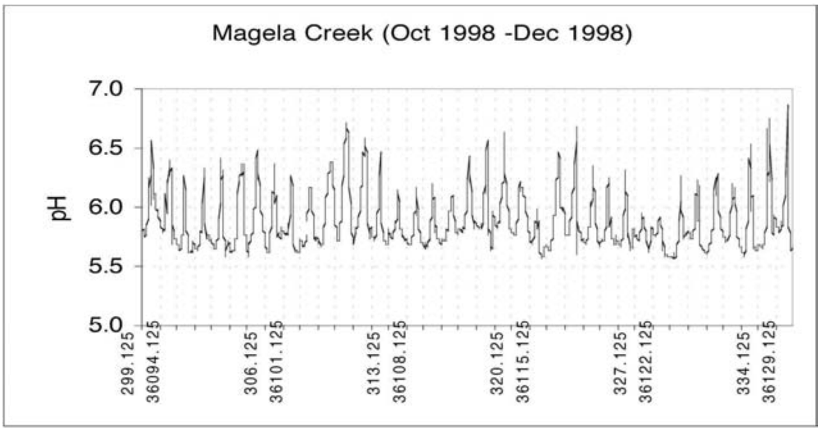

Figure 9. pH-fluctuations in the Magela Creek.

Magela Creek (Australia)

As Figure 9 shows, also in the tropical stream diurnal fluctuations of the pH occur. In contrast to the streams of the semi-arid and humid regions (Koekemoer Spruit and Lerchenbach respectively), this fluctuations take place in acidic range of pH. Starting with a minimum of about 5.6 to 5.7 (at 6:00), the pH rises during the day between for 0.5-1units to reach the daily maximum at about 16:00.

The picture changes drastically when the wet seasons starts to bring huge volumes of acidic rain water into the system (Figure 10).

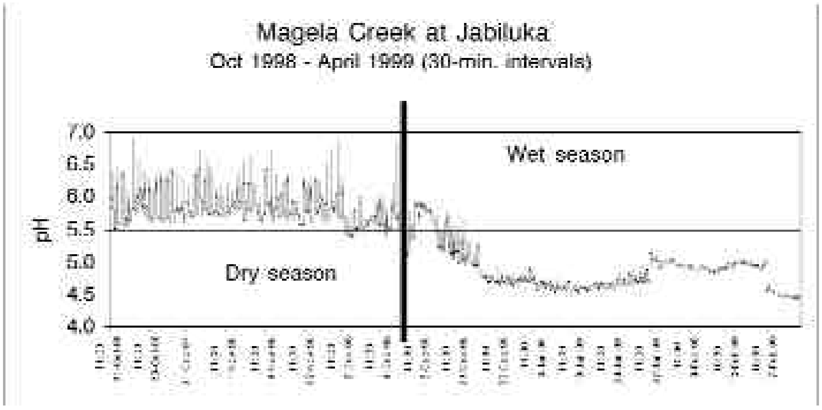

Figure 10. Seasonal fluctuations of the pH in the Magela Creek (dry and wet season).

Than the level of pH drops down to 4.5 and the amplitude of the fluctuations is reduced to about 0.2 units a day. While the greater time-interval between two measurements in the Magela Creek (30min instead of 10min) might be responsible for a slightly reduced daily amplitude, it does not explain the difference between the seasons. This is discussed in connection with the possible causes of the pH-fluctuations.

b) Causes of diurnal pH-fluctuations

According to Schwoerbel (1987), pH-oscillation in streams mainly is caused by photosynthesis of algae, phytoplancton and aquatic plants in the stream, which are using dissolved CO_2 for assimilation as soon as sunlight is available. This results in a decreasing concentration of dissolved CO_2 in the stream. Since CO_2 partly reacts with water and produces free hydrogen (equation 1-3) it affects the pH in that way, that increasing concentrations lower the pH and falling concentration brings it up:

(1) $CO_{2\ aq} + H_2O$ fl‡ $H_2CO_3^-$

(2) H_2CO_3 fl‡ $H^+ + HCO_3^-$

(3) HCO_3^- fl‡ $H^+ + CO_3^{2-}$

In addition to this free (surplus) CO_2 in water also dissolves solid $CaCO_3$ into calciumhydrogencarbonate (equation 4), which also is responsible for karst-phenomena in dolomite ($CaMgCO_3$).

(4) $CaCO_{3\ (s)} + CO_{2(aq)} + H_2O$ ‡ $Ca(HCO_3)_{(aq)}$

However, the dissolution of $CaCO_3$ only lasts until the free CO_2 is completely used and equilibrium with the dissolved calciumhydrogencarbonate is reached (“calciumcarbonate - carbonic acid – equilibrium”). If than dissolved CO_2 is taken from the system the inverse process occurs to keep the equilibrium. I.e., dissolved $Ca(HCO_3)_2$ precipitates as solid $CaCO_3$ (equation 5). Due to the associated extraction of dissolved Ca from the water during this process it is also called “de-calcification” (equation 5):

(5) $Ca(HCO_3)_{(aq)}$ ‡ $CaCO_3$ (precipitating) + $CO_{2(aq)}$ + H_2O

When photosynthesis is the main reason for the process it is termed “biological decalcification”. Apart from consumption of CO_2 by photosynthesis changes of water-temperature and/or atmospheric partial pressure of CO_2 also can reduce the concentration of dissolved carbondioxide in the water. Details of this process are discussed later. If the lack of CO_2 in the water is caused by temperature- or pressure-driven exhalation of carbondioxide the process is termed “chemical decalcification”.

The observed diurnal cycles of pH in all streams have to be seen as a consequence of mainly biological decalcification. Triggered by sunlight, photosynthesis starts soon after sunrise and reaches the maximum 3-4 hours after insolation peaked. During sunrise and pH-maximum the (biological) demand of dissolved CO_2 by green plants for photosynthesis is bigger than the (chemical) supply, which simultaneously occurs with the calcite-precipitation (equation 5). This results in an ongoing decrease of the CO_2-concentration in the stream that simultaneously causes the pH to rise (equation 1-3).

With increasing insolation, photosynthesis and the associated de-calcification increases as well. I.e., while the demand for CO_2 increases simultaneously the precipitation of CaCO3 sets increasingly more CO_2 free. However, until the pH-maximum at about 16:00 is reached, the demand for CO_2 still is bigger than the supply. It is only after this point in time that the insolation driven photosynthesis decreases so much, that the supply of CO_2 is higher than the demand by green plants and algae. This results in higher total carbondioxid concentrations and hence a gradually decreasing pH (Figure 11).

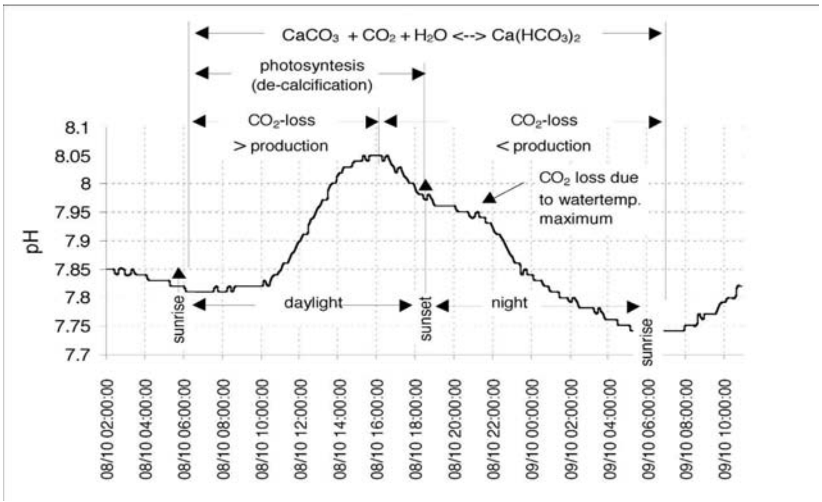

Figure 11. Processes responsible for the diurnal cycle of the pH in stream water (example from the Koekemoer Spruit, South Africa).

Because of the dolomitic origin of the water the CO_3^{2+}-concentration in the Koekemoer Spruit is comparably high. Thus, the biological consumption of CO_2 can quickly be compensated by dissociating $Ca(HCO_3)_2$ in which CO_2 is chemically "stored". This fairly high concentration of $Ca(HCO_3)_2$ in dolomitic waters results in an enhanced capacity to keep the pH stabile ("buffer capacity"). Hence, the magnitude of photosynthesis triggered pH-fluctuations in the Koekemoer Spruit is comparably low. In the Lerchenbach, however, with a non-dolomitic catchment, the pH fluctuates with up to 2 units per day, which is much more pronounced.

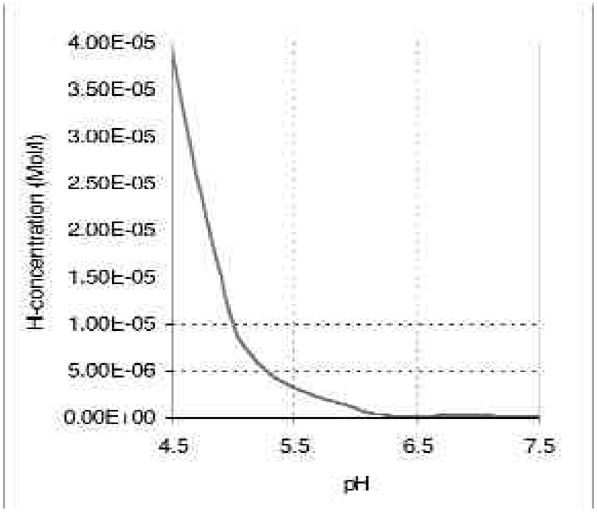

Figure 12. pH-H+-concentration.

Although the pH-fluctuations in the Magela Creek seem to be rather moderate, one has to take into account the absolute pH-level. Since the pH is a logarithmic value, changes in the lower (acidic) range comprise a significant higher amount of H^+-ions than those in the alkaline region. In fact, the small pH-fluctuation of 0.2 units during the wet in the more acidic range (pH 4.5-4.7), comprise more than double as much H^+-ions than the pH-change of 0.4 units from 5.6 to 6.0 (Figure 12). The latter, in turn, is comparable to the amplitude of pH-fluctuations found in the Lerchenbach.

In addition to the stated parameters in the Magela Creek, also the oxygen-concentration was recorded. The comparison between the pH and the O_2-chart shows that the pH-maximum coincides with the O_2-maximum. This, in turn, is evidence for photosynthesis being the major process responsible for the pH-fluctuations. While the pH-maximum indicates the CO_2-minimum, which is caused by a maximal demand by green plants and algae, it indirectly also suggests that photosynthesis reached a maximum. The same is indicated by the maximum of O_2, which is a (by-)product of photosynthesis (Figure 13).

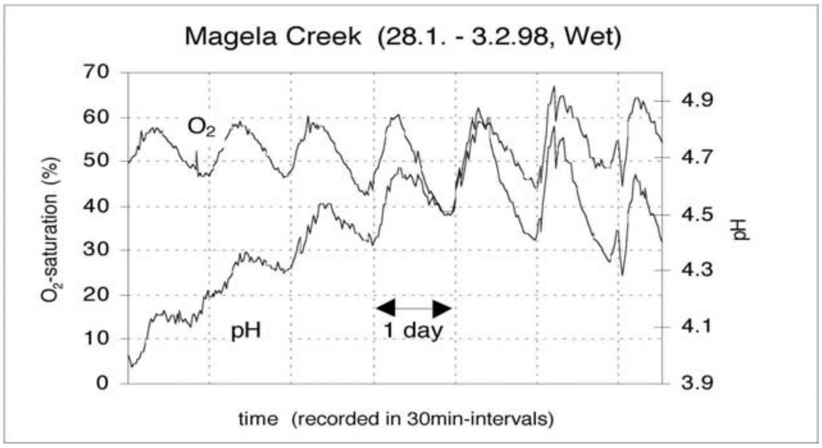

Figure 13. pH-O2 relationship in the Magela Creek (28.1.-3.2.1998).

The consumption of CO_2 not only affects the pH but also shifts the calciumcarbonate-carbondioxide-equilibrium [$CaCO_3$ + CO_2 + H_2O fl‡ $Ca(HCO_3)_2$] to the left hand side, thereby favouring the precipitation of dissolved $Ca(HCO_3)_2$ as solid $CaCO_3$. This in its turn generates free CO_2, which is “stored” in the calciumhydrogencarbonate. This process is called “biological de-calcification” because it is triggered by biota and leads to lower calcium-concentrations in the water. It starts as soon as photosynthesis begins to reduce CO_2-levels in the stream. That means that simultaneously with the consumption of CO_2 by green plants the gas is generated by de-calcification, which buffers the CO_2-loss in the stream. As long as the biological CO_2-consumption is higher than the (chemical) CO_2-generation the pH rises. It is only with decreasing photosynthetic activity in the late afternoon that chemical CO_2-generation compensates and eventually exceeds the loss. Because of its dolomitic origin the water in the Koekemoer Spruit is highly saturated with dissolved $Ca(HCO_3)_2$ constituting a “chemical reservoir” for CO_2. Due to this high “buffer capacity” of dolomitic waters biological induced pH fluctuations are comparably low, usually not exceeding 0.3-0.6 logarithmic units a day. In contrast to this in a non-dolomitic stream of the Wismut area (Germany) pH-oscillations of up to two units a day (100times H^+-concentrations!) were found (Winde 2000).

Apart from photosynthesis also water temperature affects the concentration of dissolved CO_2 by reducing the solubility of the gas when rising. Thus increasing water temperature causes decreasing CO_2-levels. Since both, photosynthesis and water temperature, are delayed reflections of insolation-intensity in “normal” streams they oscillate in an almost identically rhythm. Therefore it is likely that their effects on the CO_2-concentration amplify each other. However, this is not the case in the Koekemoer Spruit. There the maximum of the water temperature often only is reached late at night due to the elevated temperature of the deep groundwater and flow peculiarities of the pumping scheme (Winde 2001b). The effect of this delayed temperature maximum on the pH manifests itself as a second pH-maximum at night or – if not strong enough – as a “shoulder” in the pH-graph (figure 6). Instead of a further decrease due to the de-calcification (which works towards the equilibrium state of the system) this shoulder indicates the temperature induced loss of CO_2, which keeps the pH stabile (buffer effect).

As stated above the concentration of dissolved CO_2 not only depends on photosynthesis but also on water temperature. Since rising water temperature causes decreasing solubility of gases in general (Matthess, 1990, 174), the concentration of dissolved CO_2 drops as water-temperature approaches the daily maximum. Simultaneously with the dropping CO_2-level the pH rises. Hence, the daily temperature maximum in the stream should coincide with the daily pH-maximum. This, however, is not quite the case in the KMS. Instead, the pH reaches its maximum usually several hours before the water temperature does (Figure 14).

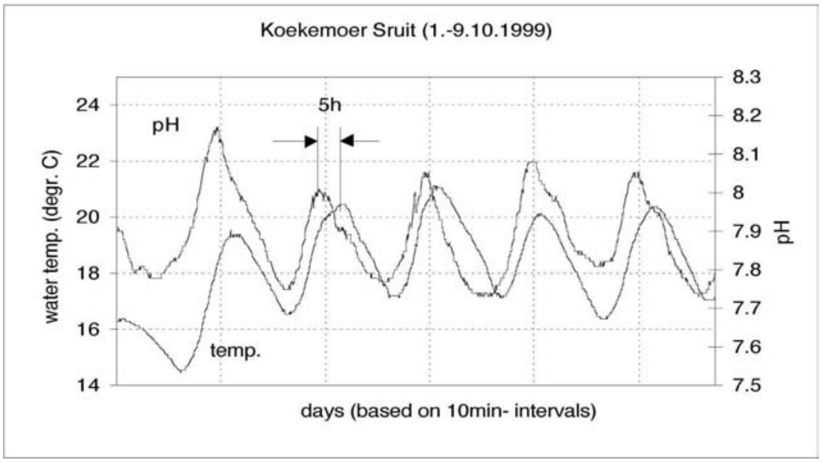

Figure 14. Tw-pH-relation in the Koekemoer Spruit (October 1999).

The maximum of the water temperature occurs – depending from the season – between early and late afternoon during spring and summer. Its oscillation follows that of the air-temperature with a delay of 2 to 5 hours, the shorter time-lag occurring in summer, when insolation intensity is higher. In autumn, however, the stream often shows the highest water temperature only during the night.

The reason for this exceptional behaviour of the water temperature maximum is the fact, that the Koekemoer Spruit mainly consists of groundwater, which is pumped from a depth of about 1–1.3km. Due to the geothermal gradient the water is already comparatively warm when it arrives at the surface. During certain days, when insolation is not strong enough to rise the temperature of the groundwater any further, the water cools down while flowing in the stream channel. To run from the outlet of the pump to the point of measurement (some 10km) takes about 12h. Because the cooling effect shrinks with increasing insolation, it usually reaches a minimum round about noon, when sun intensity is maximal. Therefore, the groundwater that is pumped into the stream channel at this point in time, cools not as much as any water which was discharged before or after. After 12 hours this water eventually arrives round about midnight at the point of measurement, displaying the highest temperature of all water that passed this point during the day (Figure 15).

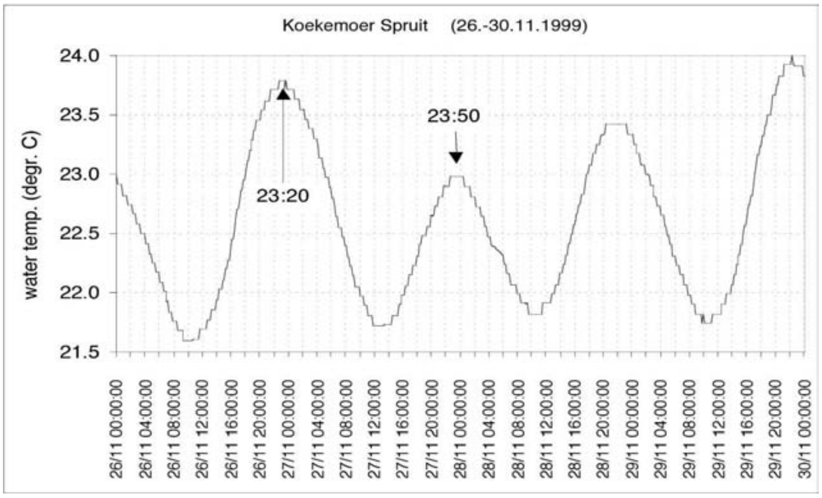

Figure 15: Water temperature regime of the KMS in spring

In wintertime, the warm groundwater cools much more rapidly so that is already cold soon after entering the stream channel. There the sun starts to warm up the water again, thereby imposing a diurnal temperature cycle on the stream. Hence the water temperature just follows the air temperature with a certain delay (greater thermal inertia of water compared to air). As a consequence of the lower insulation intensity in winter, this time gap is wider (3-4h) than during summertime (1-2h).

Since water temperature and photosynthesis are both delayed reflections of insolation intensity, in “normal” streams both parameters oscillate in an almost identically rhythm. Due to the stated mechanism, however, this is not the case in the Koekemoer Spruit. It was only due to this deviation that the impact of the water temperature on the pH in the stream could be quantified. It also is due to this deviation that overall statistical relationship between pH and water is comparably weak. In an analyses of 1200 hourly data from October/November 1999 the best correlation occurred when the water temperature was set 3h before the pH than explaining some 55% of the pH-variation. (In order to analyse the undisturbed system data from two rain-events during the analysed period were excluded. Without the exclusion there was no reasonable correlation between pH and water temperature at all).

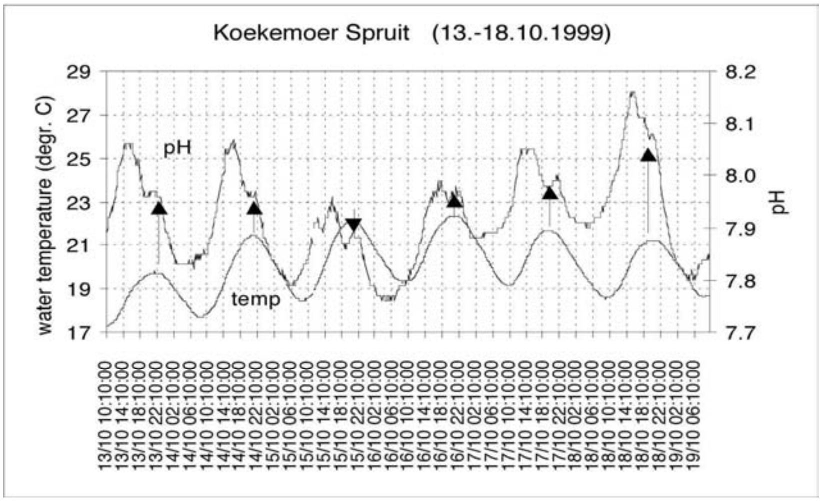

Figure 16. Second pH-max at night time due to T-max.

However, a closer look at the time series of the pH reveals that sometime a second daily pH-maximum occurs, which coincides with the temperature-maximum at night-time. This is particular obvious at the pH-cycle of the 10th, 15th and 17th October (Figure 16).

In cases where the temperature-driven rise of the pH is not strong enough to form a peak, this results in a kind of “shoulder” or plateau. This interruption of the pH-decrease lasts for several hours (Figure 16).

In exceptional cases, when photosynthesis is markedly reduced (e.g. due to a cloudy, overcast sky) the temperature-triggered pH-peak might even be higher than the photosynthesis caused one. In such cases the weak first maximum forms a “shoulder” on the left-hand side of the pH-curve. That was observed just before the rain started, pointing to impeded insolation by up-coming clouds.

It can be concluded that diurnal fluctuations of the pH in the Koekemoer Spruit are mainly controlled by the concentration of dissolved CO_2 in the water. Soon after sunrise, photosynthesis by green plants and algae as well as gradually increasing temperature cause a drop of the CO_2-concentration in the water. Both processes are shifting the calciumcarbonate-carbondioxide-equilibrium, cause a rising pH and lead to the precipitation of $CaCO_3$ (de-calcification). While in natural streams these processes take place almost simultaneously, in the Koekemoer Spruit a man-made time lag between water-temperature and photosynthesis-cycle allowed to compare their impacts on the pH. The lower temperature-driven pH-maximum during the night compared to the high pH-peak caused by photosynthesis suggests that the latter is the more important process in this regard.

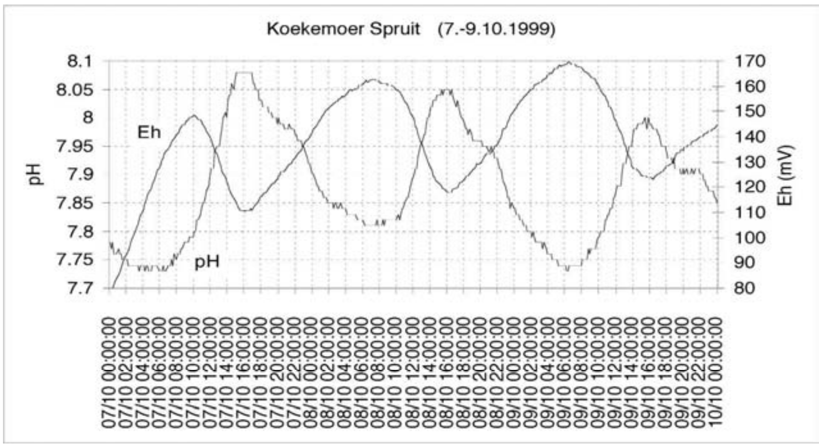

Figure 17. Eh-pH-relationship during dry weather in the Koekemoer Spruit.

Since the daily maximum of the water-temperature shifts its position during the course of the year, in some seasons temporarily superposition of both effects are to be expected. By superimposing both, biological and chemical de-calcification the pH may fluctuate more pronounced. This is most likely to happen during summer, when water temperature and photosynthesis are oscillating in almost the same rhythm.

4.1.2. Redox potential

Measurements of the redox-potential only were carried out in the Koekemoer Spruit and the Magela Creek. While the pH represents the concentration of positive charged hydrogen ions in the system the Eh reflects the concentration of electrons (e^-) as opposite charged counterparts. Figure 17 shows for the Koekemoer Spruit that Eh oscillates inverse to pH.

Since the sum of valances in a system remains constant, rising concentrations on one side (e.g. pH) implies decreasing concentration on the other side (Eh). Thus, the observed inverse relation between both parameters is plausible. An analysis based on long-term time series is, however, complicated by episodically occurring drops of the Eh, for which no explanation could be found yet. Due to these dips only a very weak statistical relation between both time series was found. However, the analysis also showed, that the best correlation (which at least is negative: -0.13) occurred when no time lag between both parameters was set. This points to immediate interactions of both parameters, indicating the mutual dependency. With amplitudes of 40-50mV per day Eh-fluctuations comprise about 11-15% of the daily maximum, usually fluctuating in oxidising regions.

4.1.3. Electric Conductivity

The precipitation of $CaCO_3$ due to the photosynthesis-controlled consumption of CO_2 also reduces the concentration of dissolved solids in the water column, measured as

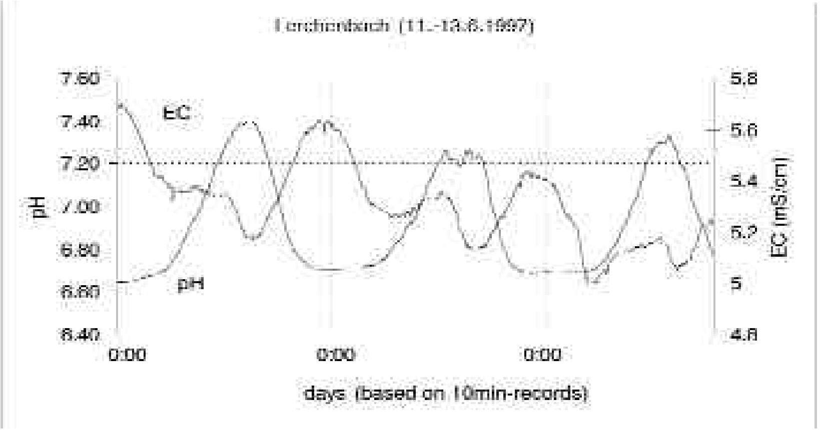

Figure 18. pH-EC-relationship in the Lerchenbach (11.-13.06.1997).

electric conductivity (EC). Thus increasing precipitation of calcite not only brings the pH of the stream up but simultaneously also lowers its EC, resulting in an inverse relationship of pH and EC.

While this type of relationship is present in the Lerchenbach (Figure 18), it could not be found in the Koekemoer Spruit.

Here the daily maximum of the EC precedes the pH maximum by several hours. In long-term time histories it even seems that there is almost no relationship between the two parameters at all. The statistical analyses of hourly data from October-November 1999 yielded best correlation when EC was set 1h ahead of pH. But even than, the pH explained only 32% of the EC-variation.

This poor relation probably is due to other factors influencing the EC stronger than the calcite precipitation does. That includes possible wastewater-inflows from the sewage plant at Stilfontein as well as from the Buffelsfontein Goldmine. This also might be the reason for a comparably uneven diurnal fluctuation, which shifts in terms of frequency as well as magnitude.

While no immediate relation to the pH could be proven, a close link of the EC to the water temperature exists. Despite a seemingly low similarity between the oscillation of EC and water temperature during the stated dry weather period, both parameters are connected with respect to their diurnal amplitudes. Comparing the differences between the daily maximum and minimum of both pH and EC reveals a significant linear correlation with R=0.8522 (Figure 19).

Since EC rises when temperature does and vice versa, this relationship is plausible (WTW 1993). However, the influence of temperature in all used EC-probes was electronically compensated to the reference value of 25° C. Therefore mere temperature fluctuations shouldn't cause any EC-variations. Since water temperature influences the position of dissociation-equilibrium, this in turn might affect the EC by shifting to a state where more free ions are available.

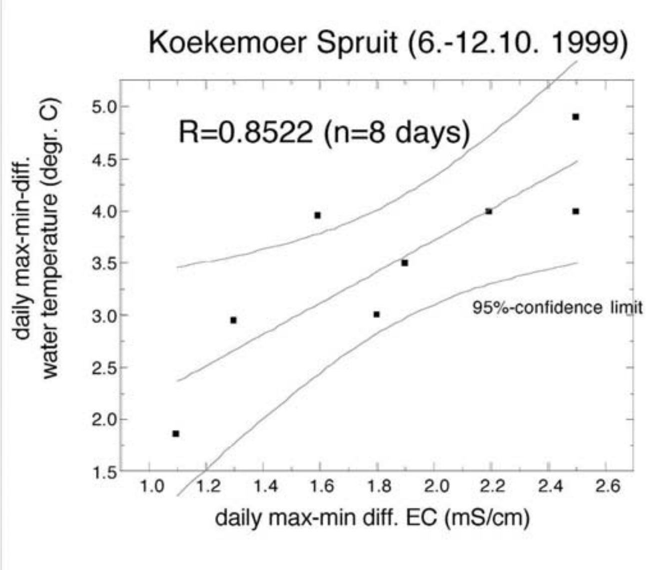

Figure 19. Linear regression between daily max-min-diff. of EC and temperature in the KMS (6.-13.11.99).

4.2. Impacts of rain events on the hydrochemistry of the stream

While it is likely that the diurnal fluctuation of the pH rather affects the rate of uranium-immobilisation in the stream than causing the re-mobilisation of uranium from sediments, this might be different in case of event-related pH-changes which often last longer and cover a wider range. Figure 20 shows an example for the effects of a rain event on the pH in the Koekemoer Spruit.

Due to acidic rainwater (a minimum pH of 3.7 in rain water was measured) the pH in the stream drops within a few hours for about 1 unit down to 6.8. Taking the diurnal fluctuation into account the pH drops, in fact, for more than 1.2 units since the decrease occurs during a time where the pH usually reaches the daily maximum (dashed line in figure 20). I.e., in cases where rainstorms coincide with the daily pH-minimum (short before sunrise) an even deeper pH-drop is likely.

Since low pH-values favour the re-solution of uranium from sediments (Wade et al. 2000) pulses of dissolved uranium in the stream as a result shortly after acid rain events are not to be excluded. This in particular is of concern in streams with non-dolomitic water, which can hardly buffer the acidic input.

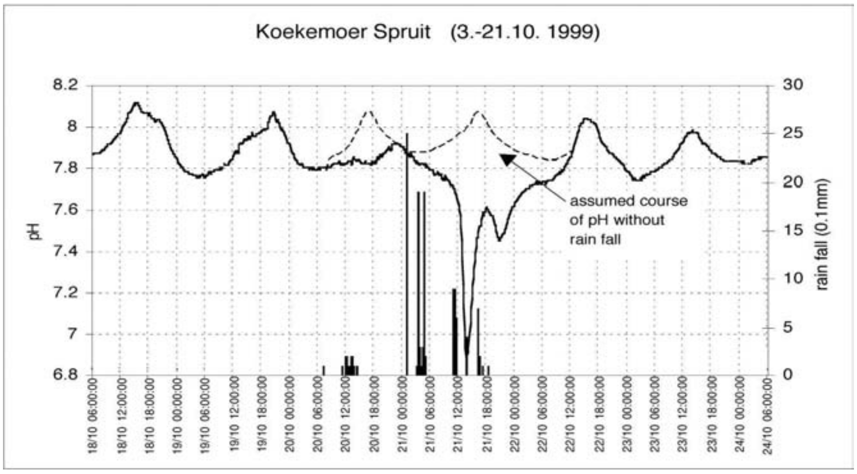

Figure 20. pH-response of the Koekemoer Spruit to rainfall.

But nevertheless it suggests that amongst volume and pH of the rainwater also the time of the day, in which the rain hits the stream, determine the magnitude of pH-drops. E.g., if the acid input had hit the stream during its diurnal pH-minimum a further drop of 0.2 to 0.4 pH-units would have been likely.

To determine the delay between the actual rainfall and the stream response the starting-time of the heavy rains (about 4:00) was compared with the time when the pH reached its minimum. The difference indicates that the stream response lags behind the rain by some 9hours. Therefore, rainstorms occurring round about 21:00, are especially likely to cause deep pH-drops since their impact coincides with the diurnal pH-low at about 6:00.

Due to the low EC of in rainwater (median from 22 samples: 0.03mS/cm) the much higher EC of the stream drops as soon as rainwater mixes in. However, in contrast to the pH and the water temperature, there are no stabile diurnal oscillations of the EC. For this reason one can hardly refer to “normal daily” minimum or maximum. Thus, the quantification of the drop, which also takes the compensation of diurnal oscillations into account, is rather difficult. Though, the first maximum after the rain certainly is below its normal level (minus 0.1mS/cm).

The EC-minimum during occurs about 2h later than the pH-minimum. This is in so far surprising as both parameters reflect the impact of rain and hence are supposed to act simultaneously. The reason for the delayed minimum of the EC is likely to be caused by stormwater overflows discharging into the Koekemoer Spruit. After the rain stopped, the EC still was for another 37 hours below normal, thereby suggesting that surface run off from the upper catchment still diluted the pumped groundwater. An increased input of shallow alluvial groundwater into the river, as possible reason for the long lasting dilution effect is rather unlikely, since the rising stream level caused infiltrating conditions in the floodplain. In addition to that, most of the alluvial groundwater actually shows a higher EC than the stream itself. Compared to 37h of the EC the pH “recovered” rather fast, showing “normal” oscillation again already 12h after the rain stopped.

4.3. Implications for mobility and fluvial transport of uranium

As found by Hellmann (1990) for the river Rhein (Germany), biological de-calcification reduces the concentration of dissolved heavy metals in stream water by precipitating them along with $CaCO_3$. The calcite often was found to precipitate as crust (“Aufwuchs”) on suspended solids.

A high correlation between the $CaCO_3$-content and the uranium-concentration in bottom sediments prove that this process takes place in the Koekemoer Spruit. It is therefore to be expected that diurnal variations in the intensity of de-calcification are reflected by diurnal cycles of the uranium/heavy metal concentration in the stream. This also is true for seasonal variations throughout the year. This on the other hand might have practical implications for downstream users to extract water preferably during times of low metal-concentration, avoiding metal-peaks.

Apart from co-precipitation with calcite the pH and Eh also affect the speciation of dissolved metals, which in turn determines their mobility. Figure 21 displays a pH-Eh-stability diagram for uranium in dolomitic water (calculated by Wade et al. 2000 using the thermodynamic speciation model JESS) which suggest, that the observed diurnal fluctuations of pH and Eh are not likely to have profound effects on speciation changes. However, in terms of re-mobilisation the diagram suggests that a pH-drop below 6 (under normal oxidising conditions) might allow for uranium to stay in solution as $(UO_2)_3OH^{5+}$ instead of precipitating as a carbonate.

In general, effects of Eh-changes on the uranium mobility in the stream are likely to be rather small compared to pH. Apart from controlling the calciumcarbonate-precipitation, the pH also affects the precipitation of iron- and manganese-oxides/hydroxides, which was identified as another important mechanism of uranium immobilisation in the Koekemoer Spruit (Winde 2001a). E.g. the rate of iron(III)hydroxid precipitation increases a 100 times if the pH [and thus the (OH)—concentration] rises by only half a logarithmic unit (Matthess, 1990).

In addition to this, the precipitation of inorganic Fe(II) as $Fe(OH)_3$ - without bacteria - only is possible in a neutral-alkaline environment with pH>7. The precipitation of Mn as hydrous oxide or oxide (MnO_2) needs even higher pH-values (>8.5).

Beside the co-precipitation of uranium with the said compounds, also its subsequent adsorption onto the precipitation-products is ruled by the pH. For example the surface-charge of hydrous iron-oxides only turns negative (and thereby being receptive for cations) when the pH rises above 8.0. As long as the pH is lower, no adsorption of uranium onto the precipitated gels, which is regarded as an important immobilisation process (Wade *et al.*, 2000), can take place.

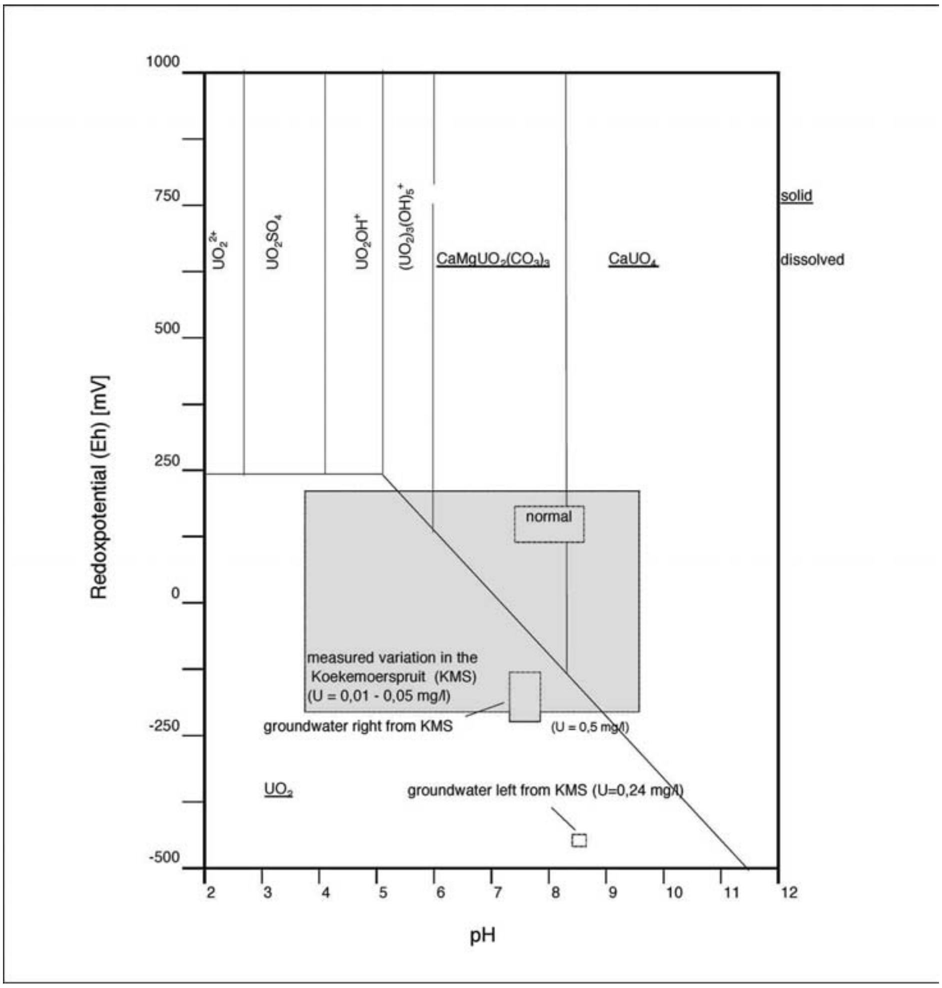

Figure 21. pH-Eh-stability diagram for uranium (1uM) in dolomitic water (adapted from Wade et al. 2000).

Comparing the given thresholds with the pH-range covered by diurnal fluctuations in the Koekemoer Spruit and the Lerchenbach, a number of stated immobilisation processes only take place during certain times of the day. This is likely to contribute to changing metal concentrations during the day. Since alkaline conditions with pH-values close to 8 in general favour the occurrence of precipitation and adsorption a lower concentration of dissolved uranium during the afternoon is to be expected. This, however, is not true for the tropical system, were the pH of the stream water stays well below 7 throughout the year. Under dominating acid conditions no stronger immobilisation of uranium by precipitation or adsorption is to be expected. This is confirmed by very low uranium concentrations of the sediments in the Magela Creek after passing Ranger Uranium Mine.

While precipitation happens rather fast (within minutes), the re-solution of precipitated compounds in general is a much slower process (Matthes, 1990). Thus it is to be expected that the fluctuating pH rather affects the rate of uranium immobilisation in the stream than causing the release of uranium from sediments by re-solution. This might be different in case of event-related pH-drops, which often last longer and cover a wider range. The latter is of particular concern in streams with non-dolomitic water, which can hardly buffer the acidic input.

5. Synoptic summary and conclusion (part I – part III)

By chemical analyses of water and sediments samples from the Koekemoer Spruit, the significance of tailings deposits from gold and uranium mining (termed slimes dams) as source of waterborne stream contamination could be established. Dissolved uranium and other heavy metals move along with seepage from the tailings deposits into the groundwater which finally seeps diffusely into the Koekemoer Spruit. A rapid increase of the uranium concentration in the slimes dams, resulting from abandonment of uranium production by many mines, significantly elevated their potential for stream pollution.

On its way to the stream, uranium passes through several sediment-water systems where different mechanisms partly remove the dissolved metal from the water column by turning it into solid phases (immobilisation). In the fluvial system precipitation of calcite (de-calcification) and iron-manganese hydroxides are the most important mechanisms for immobilising uranium. The latter process in particular happens in the bottom sediments of the stream channel. As interface between reducing groundwater and oxygenated streamwater, the interstitial act as kind of a geochemical barrier for dissolved uranium and other heavy metals. Because of the protection from the flowing water, the precipitating gels can accumulate in the sediment-pores and crystallise over time to solid constituents.

While retaining uranium helps to reduce waterborne stream-contamination, it simultaneously contaminates the affected sediments. They, in turn, may act as a secondary source of contamination, as e.g. it was found for sulphate crusts on floodplain sediments. Containing extreme high uranium concentrations these crusts are easily re-soluted by rainwater running into the adjacent stream.

Since alluvial groundwater is the main source of uranium-contamination of the Koekemoer Spruit, the actual stream pollution not only depends on the concentration of uranium in the groundwater but also on the volumes (rate) in which it infiltrates into the stream. This in turn is largely controlled by pronounced diurnal fluctuations of gauging heights in the stream channel, which result from a pumping scheme. By causing even higher fluctuations of the groundwater level in the adjacent floodplain, this results in highly dynamic stream-groundwater interactions, including daily turn-arounds of the direction of flow between both water bodies over certain times of the year, allowing for contaminated groundwater to seep into the stream only at night. The latter creates a need to adapt current monitoring protocols to these dynamics. Apart from this the man-made modifications of the hydraulic system also may lead to more frequent redox-initiated precipitation of uranium in the floodplain sediments, changing from wet (reduced) to dry (oxidising) conditions daily.

Once uranium is discharged into the stream the rate of downstream transport mainly depends on the speciation, which determines whether it stays in solution or gets immobilised by turning into a solid phase. This again is depending mainly on pH and Eh of the stream. For both parameters, pronounced diurnal fluctuations were found, triggered by photosynthesis and water-temperature based shifts of the calciumcarbonate-carbondioxide-equlibrium. Influenced by regional pecularities (geological formations, rainwater chemistry, aquatic vegetation, day-night rhythm and the season) these fluctuations vary in amplitude and the covered range of pH. While dolomitic stream water in the Koekemoer Spruit constitutes a well buffered (alkaline) system, which only allows an amplitude of about half a pH-unit, the pH of the Lerchenbach oscillated with up to two units a day, thereby significantly changing the chemical conditions for uranium transport. E.g., the rate of precipitation of iron as $Fe(OH)_3$ – which is known for co-precipitating uranium as well - increases by a factor of 100 for each rise of the pH by only half a unit. I.e., in the Lerchenbach the rate rises during the day by 10^8 times, suggesting pronounced diurnal difference in the immobilisation rate and thus the water pollution with uranium. Apart from precipitation, also adsorption processes are strongly pH-depended. Manganese oxides for example, only show negative charged surfaces if the pH is > 8.0. thus it is to be expected that the concentration of dissolved uranium in the stream is subject to fluctuations caused by pH-oscillations.

In the Koekemoer Spruit the daily fluctuation of the hydraulic groundwater input and the oscillation of stream chemistry are overlaid rather unfortunate. Since groundwater preferably seeps into the stream during the night, when no photosynthesis occurs, it mixes with stream water with comparably low oxygen concentration. With simultaneously low pH-values during this time, a comparably poor immobilisation rate is to be expected. Therefore it is likely, that dissolved uranium from the in-seeping groundwater mainly stays in solution.

Although the amplitude of the pH-fluctuations in the acidic waters of the Magela Creek seems rather small, they, in fact, comprise the same or even higher amounts of hydrogen ions as pH-changes in the alkaline range. Since acidic conditions in general don’t allow for extensive precipitation the influence on the uranium transport is expected to be rather small. In addition to this, also diurnal oscillations of the Eh and the EC were observed, which not always show consistent relationships to the pH-changes. In general the Eh-fluctuations are likely to affect the uranium-speciation less than the pH.

In conclusion resulting uranium transport in streams is determined by the net effect of the superimposing of both processes: the man-made fluctuations of the hydraulic stream-groundwater interaction (where applicable) and diurnal hydrochemical oscillations of the stream water. In addition the system is exposed to event-related changes of streamwater chemistry. In this regard acid rainfall is of particular concern, since it leads to more acidic conditions in the stream which in general favour re-mobilisation and high mobility of uranium. This is of particular concern in streams with low buffer capacity, where the rain-triggered drops of the pH are deeper and last longer. However, the main effect of diurnal and event related pH fluctuations is not to re-mobilise solid uranium from sediments, but preventing dissolved uranium from being immobilised.

Acknowledgements

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