

Interview with Dr. Thomas Riedel

Hello Thomas. Thank you very much for making time for our interview. You are an expert in ground- and drinkwater quality management. Therefore we prepared some questions about manganese in groundwater, since this is of high relevance and interest for this year's iGEM Tübingen project.

In your paper "Temperature associated changes in groundwater quality" you describe that you found an increasement of manganese in the local groundwater. How can this be explained or where does it come from?

First of all, it should be noted that manganese is very common in the upper earth crust. Since it is very easily involved in redox reactions, it can be present in various oxidation states, whereby in nature only the oxidation states +2, +3 and +4 occur. While manganese(II)ions are often dissolved in ground water or sorbed on mineral surfaces, manganese(III)ions are often bound to organic acids. Manganese(IV)ions on the other hand are present as manganese oxide. How the manganese concentration rises with rising temperatures in the groundwater cannot be explained beyond doubt at present, but it has been known for some time that manganese tends to dissolve more easily at temperatures above 10 °C. Mechanistically this can be explained by the fact that the microorganisms that breathe manganese become active. However, the details of this process are still largely unknown, as these microorganisms are difficult to cultivate in the laboratory. What is known however, is that these organisms are facultative aerobes that breathe manganese when the temperature limit of 10 °C is exceeded.

It is clear that bank filtrates, i.e. water obtained from wells located close to rivers or lakes, have a lower manganese concentration when temperatures are low in winter and a higher concentration in summer when temperatures, and therefore the rate of microbial manganese respiration, increase. However, these statements can only be supported by the data collected in Baden-Württemberg. Whether this is valid worldwide is not so easy to clarify. Also, because many details of this process are still in the dark, it cannot be ruled out that the increasement in manganese concentration in groundwater must be attributed to a much more complex interplay of various factors. It is also conceivable, for example, that an increase in water temperature could lead to more organic compounds dissolving and thus stimulate the metabolism of these manganese-breathing microorganisms. The increase in manganese concentration does not necessarily have to be due to industrial reasons, but it is also known that manganese concentration is higher near the agglomerations of certain industries, as anthropogenic causes are added to the natural causes.

The real problem with manganese oxides, apart from their toxicity, is that they can react with a variety of other elements, including various heavy metals, such as vanadium, which then also go into solution.

It is no surprise that an increased concentration of dissolved manganese is detectable in Baden-Württemberg, because as soon as reducing conditions are available, many microorganisms switch to manganese respiration. These conditions exist mainly in and around swamps and in the vicinity of hydromorphic soils, i.e. areas where the groundwater level is very close to the surface. This is particularly the case in northern Germany, but also in areas of the Netherlands, Denmark, Poland and large parts of the Baltic States.

Do you see this increase as worrying?

No, in fact not in Germany. The standards of water treatment and quality management here are so high that there is no need to worry about this increase in terms of drinking water quality. There are corresponding techniques that allow the water to be freed from manganese oxides by a filter system by precipitating them through the filtration process. Manganese(II)ions oxidise slowly to manganese(IV)ions in the presence of oxygen and then precipitate as MnO_2 . In waterworks, an oxidant is often added to accelerate the precipitation of manganese oxides. It becomes a problem when these techniques are not available.

Would you say that the contamination of water reservoirs with manganese will be a serious problem not only in developing countries but also in Germany in the long term and especially in the German state of Baden-Württemberg?

As already mentioned, there is no reason to worry in Germany, since the standards for water treatment and drinking water monitoring are very high. The limit value that must be met is $50 \mu\text{g/l}$. If this is exceeded in the future, this will not present us and the drinking water suppliers with insoluble tasks either, as increased manganese concentrations can be reduced by adding a deflocculant.

The situation may be different on a smaller scale, such as in the case of domestic wells, which are not regularly monitored. In individual cases, it may well be that the limit value for manganese is exceeded.

A MAK value of 0.02 mg/m^3 applies to manganese dust. What is the limit value for manganese in water and how is manganese normally detected by hydrological methods?

A limit value of $50 \mu\text{g/l}$ applies to drinking water. Accordingly, this limit value does not apply to natural systems, such as moorlands, where high manganese concentrations are normal.

Optical emission spectrometry (OES) has established itself as the standard method for detecting certain substances in water samples as this method is relatively inexpensive, especially compared to mass spectrometry, and the given detection limit for manganese can be achieved very well. However, if substances in the nanogram per litre range need to be detected, mass spectrometry is the most suitable method.

How sensitive are these optical methods? Are there any limits with these methods?

The OES devices have become very sensitive in the meantime, although it should be noted that the advantages and disadvantages of such a device depend mainly on the application context and the resulting objective. A scientist who is interested in the exact composition of a sample is likely to work significantly differently with the same instrument and also get more specificity out of it than a large analytical laboratory where a large number of samples have to be analysed on a daily basis for a certain concentration.

In our iGEM project we are working on a biosensor for the detection of manganese ions. This sensor has reached a detection limit of 10 micromol/l in previous works and is inferior to the established detection methods in terms of sensitivity. Do you have an idea how the sensitivity of the detection via the biosensor could be increased by combining it with established methods?

The detection limit of the biosensor is a factor of ten above the limit for drinking water in Germany, which makes it rather uninteresting for this application. However, its applicability always depends on how the limit values are determined. For example, the WHO set a limit value of 500 g/l from 1993 until it was changed again. This would be a concentration that could still be detected by a biosensor. However, it may well be sufficient, for example in structurally weak areas, to have a simple and inexpensive way of determining whether the given manganese concentration is above or below a critical value, or of the approximate magnitude of the concentration, without having to make an exact quantification. Therefore, even though the project may not be able to keep up with standard technical methods, it is definitely a justified approach.