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Redox Reactions in Groundwater with Health Implications

Gunnar Jacks

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Abstract

Mobilisation into groundwater of many trace elements are redox dependant and of health concern. A short list includes arsenic, manganese, chromium, selenium, nitrogen as nitrate and uranium. Arsenic is mobile in groundwater essentially under two conditions, under reducing conditions mobilising ferrous iron and arsenite and at high pH when the ferric oxyhydroxides lose their positive charge. Manganese is mobilised under moderately reducing conditions as Mn^{2+} and might affect the mental capacity at chronic exposure from drinking water. Chromium is mobile as carcinogenic chromate under oxidising conditions. Manganese oxides may oxidise Cr(III) solids. Chromium may come from natural as well as anthropogenic sources. Selenium, an essential element, rarely exceeds permissible limits but irrigation with groundwater with elevated selenium could cause toxic selenium intake via food. Selenium is mobile in groundwater under oxidising conditions. Nitrate from excess use of fertilisers may be a problem for bottle-fed children below the age of 1 year, forming methaemoglobinemia. Uranium is mobile under oxidising conditions as U(VI). Mobility and toxicity depends on numerous factors. The threat from uranium is its effect on the reabsorption in the kidney of water and salts from the primary urine. Oxidation state and speciation govern uranium mobility.

Keywords: redox, groundwater, trace elements, mobility, health

1. Introduction

Groundwater is by far the largest fresh water resource on the globe. It is often a safe drinking water source from bacteriological point of view, and the development of safe wells in many countries has saved millions of children in particular. However, the development of deeper sources of groundwater has implied redox reactions that may mobilise elements that are toxic, such as arsenic and manganese. Other elements of health concern whose mobility is redox-dependant

may be introduced from natural and/or anthropogenic sources such as chromium, uranium and nitrogen. This contribution will present the processes behind the mobility with examples from hydrogeology and hydrochemistry on a global scale.

To get a simple overview of the redox reactions in nature a so-called aerobic/anaerobic staircase including only major redox-sensitive species in groundwater could be used (**Figure 1**). In reality, the 'steps' are numerous if all elements, including trace elements are taken into account.

While pH is related to the activity of protons, Eh or redox potential is related to the activity of electrons (**Figure 2**). To define a specific redox level, Eh measurements with a platinum electrode and a reference electrode, commonly an Ag/AgCl electrode, are helpful but often difficult to interpret [1]. However, it is essentially the Fe(II)/Fe(III) couple that can be relied upon provided the concentrations of both species are not too small. Most redox measurements mirror a mixed potential [2]. Many species are not electrically active at the platinum electrode. ZoBell's solution is commonly used to check the electrodes [3]. The redox potential should preferably be measured in a so-called flow-through cell to avoid any air to come in contact with the groundwater. Speciation of the form of the elements is another tool that can be applied for instance for separating As(III) from As(VI). Numerous methods of speciation are published (e.g. [1, 4]).

In general, the species that are more mobile are anions as the cations in the form of most heavy metals are quite strongly adsorbed to clay minerals and organic matter at around neutral and alkaline pH while anions, adsorbed onto ferric oxyhydroxides and aluminium compounds, are less adsorbed at moderately alkaline conditions and not at all above zero points of charge (ZPC) (**Figure 3**) which is at a pH of 8.2 for ferric oxyhydroxides. Reducing conditions with the reduction of ferric iron to soluble ferrous iron is another case of the failure of adsorption of anionic species.

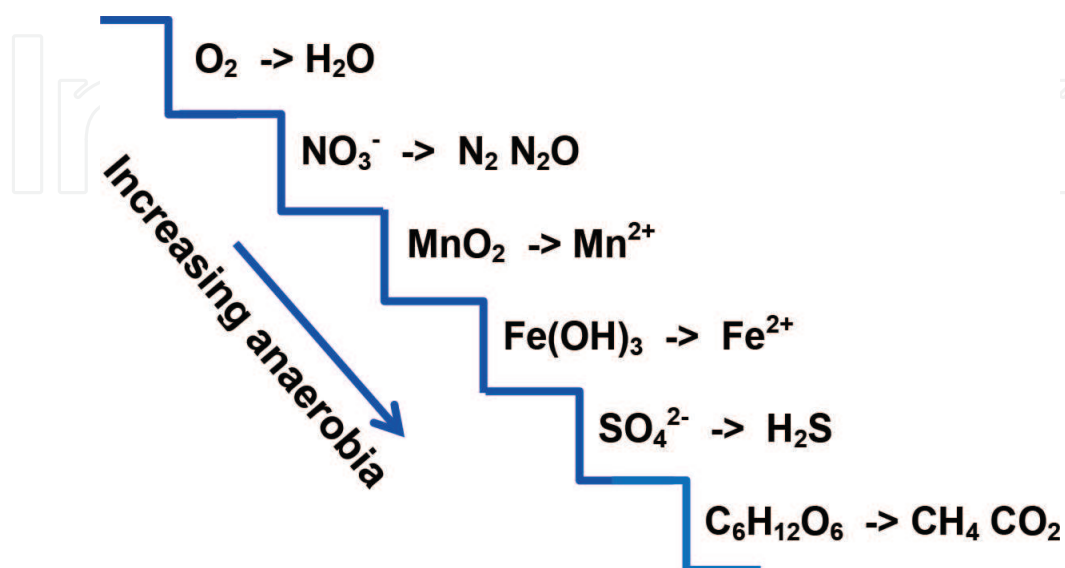


Figure 1. The aerobic/anaerobic 'staircase' for major elements in groundwater.

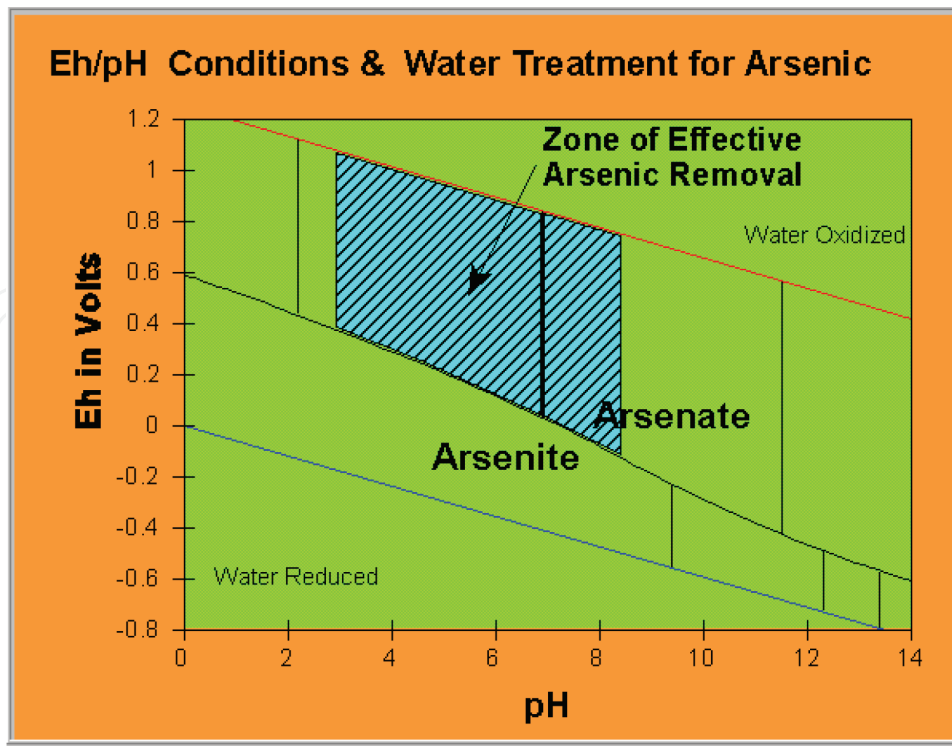


Figure 2. The Eh-pH diagram for arsenic with an overlay of iron.

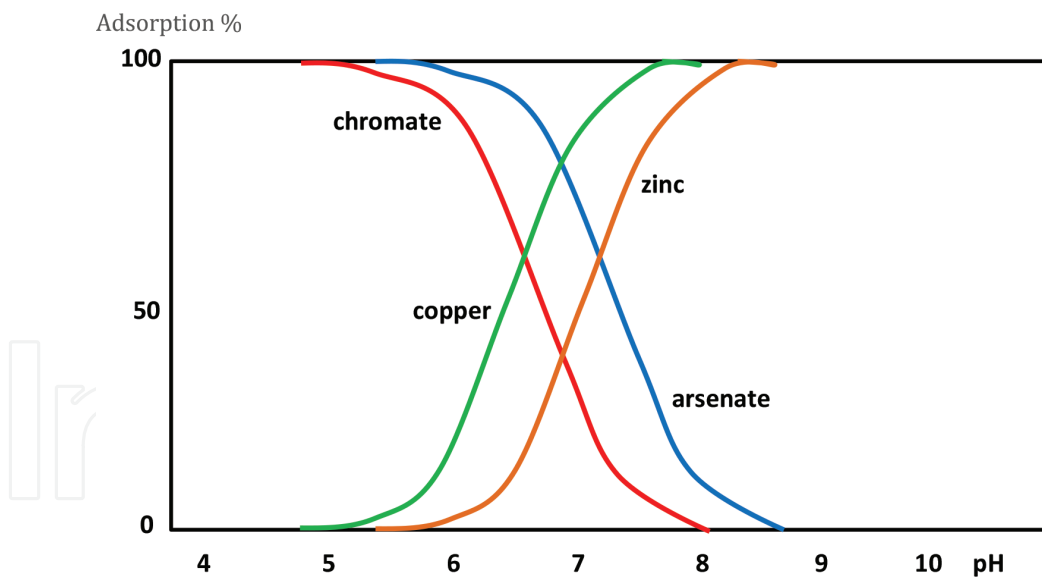


Figure 3. Adsorption of cationic and anionic species.

2. Arsenic

Arsenic is an element that has been known and used by mankind since the Bronze Age to make bronze stiffer. It has been introduced in society for different purposes such as for the removal of air bubbles in glass in medieval times. In the eighteenth century, it was used to cure different ailments. Its toxicity has been known for long time. A step forward in detection

of low concentrations of arsenic was done by Berzelius, a Swedish chemist, who invented a qualitative but sensitive analysis [6]. Arsenic in groundwater has been known for quite some time; however, an extensive epidemiological investigation warranted the lowering of the safe level from 50 to 10 $\mu\text{g/l}$ by WHO and that was adopted in most countries.

Arsenic is mobile in groundwater under two conditions, in a reducing environment as arsenite (As(III)) and in an oxidising environment at elevated pH as arsenate As(V) . The mobility is closely related to the chemistry of iron oxyhydroxides. Under ferric-reducing conditions, the arsenite adsorbed onto the ferric compounds is released when the adsorbent is mobilised as soluble ferrous iron. Under oxidising conditions, the arsenate is mobilised at pH above 8.2, the ZPC for ferric oxyhydroxides.

In the 1990s, it was discovered that groundwater in many aquifers in south and southeast Asia had levels of arsenic that threatened the health of millions of people. In the Bengal delta in Bangladesh, 35–75 million people are exposed to excess arsenic depending on whether the 50 or the 10 $\mu\text{g/l}$ level limit is used. Symptoms of arsenicosis were seen by a doctor in West Bengal in India and groundwater analysis showed high contents of arsenic [7]. In Bangladesh, the child mortality was high before the 1960s due to the use of bacteriologically polluted surface water. The switching over to cheap wells down to a depth of ~30–50 m meant a radical decrease in mortality but after 10–15 years, the slow poisoning with arsenic from those wells became evident. The discovery evoked a discussion about the mechanisms behind the elevated levels of arsenic amounting even up to mg/l . An initial hypothesis was that the introduction of wells had lowered the groundwater level and allowed oxygen to diffuse into the sub-ground level causing oxidation of arsenopyrite (**Figure 4**). However, a common feature of the polluted groundwater was high contents of dissolved iron and it turned out to be a completely internal process in the sediments where organic matter degraded under anaerobic conditions by bacteria using ferric iron as an oxidant dissolving ferric oxyhydroxides, releasing arsenic in the form of arsenite into the groundwater [8] (**Figure 4**). The arsenic content in the sediments is moderately higher than elsewhere due to sources like rocks in the Himalayas [9]. This is, however, not the cause for the mobilisation of arsenic in the groundwater in the Bengal delta and the Gangetic plain; the redox level in the sediments is the reason.

Further work has shown that deeper wells are safe with a higher redox level than the shallower. This can be traced back to glacial times. The sediments deposited during Pleistocene, before the last glacial maximum (LGM) when the sea level was lowered at a geologically rather fast rate,

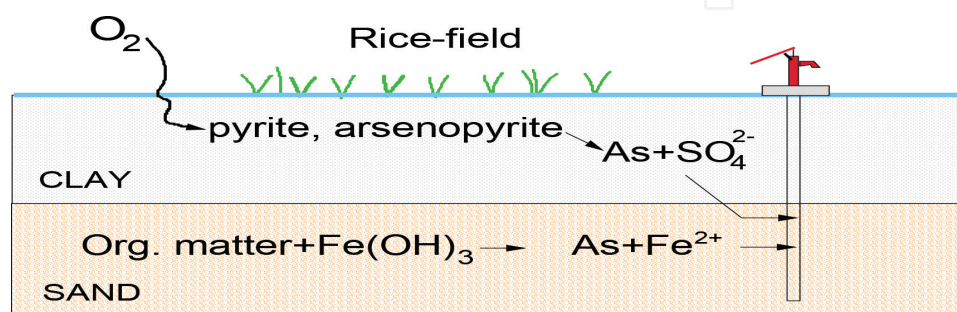


Figure 4. A hypothesis regarding the mobilisation of arsenic in the Bengal delta.

were deposited under rather oxidising conditions, and they were due to the lowering of the sea level subject erosion and re-sedimentation. Contrary, after the LGM when the sea level rose, there was more formation of wetlands allowing the introduction of more organic matter in the postglacial sediments.

While the removal of arsenic from the groundwater functions technically, it does not work socially as women who are expected to handle the filters are too burdened by daily tasks [10, 11]. However, it has been found that safe sediments can be identified by their colour. This is a practice that was found out by local drillers in search for low-iron groundwater. What they did not know was that low-iron groundwater is also low in arsenic (**Figure 5**) [12]. The colour code tool has been developed from a large number of sediment samples paired with many groundwater analyses. The colour scheme that has been used is the Munsell Colour code [13]. As indicated above, the Pleistocene sediments at around 100 m depth were likely to be a good target. The colour code was tested on 243 wells drilled to around that depth [14]. The prediction of safe groundwater below 10 µg/l is 91%, while low manganese, below WHO's technical guideline at 400 µg/l, can be achieved in 89% of the cases [14].

Another colour tool mirroring the redox conditions in the groundwater is the colour of the platforms at hand pumps in the Bengal delta [15]. Red precipitates of ferric hydroxide indicate an iron-reducing groundwater which has often, in the Bengal delta, elevated arsenic concentrations. A black platform with precipitates of manganese oxides mirrors a higher redox level where the arsenic concentrations are lower.

Another mechanism of mobilisation of arsenic may occur under oxidising conditions at an elevated pH above the ZPC of the major adsorbents, ferric oxyhydroxides of different types.

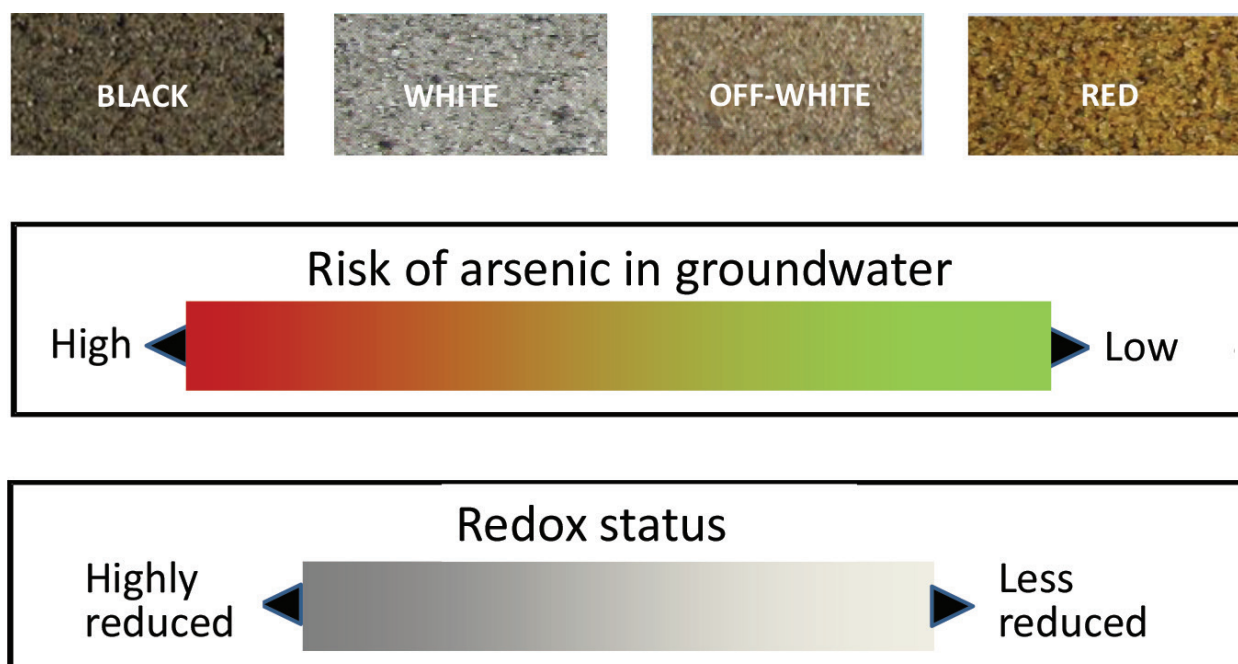


Figure 5. A simplified colour code to identify low arsenic groundwater in the Bengal delta [12].

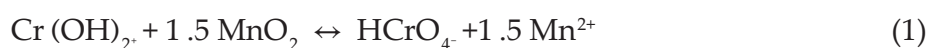
This is common in the Andes in South America [16]. The arsenic is then present as arsenate, and the high pH of groundwater tends to be of the Na-HCO₃ type [17].

3. Manganese

Manganese in groundwater has been considered as a technical problem causing blackish flushes in tap water after oxidation of the Mn²⁺ to Mn oxides in the distribution networks. Manganese inhaled from air has neurological effects known from metallurgical industries [18]. Recently, however, reports have come to indicate that chronic exposure of children to manganese in drinking water may affect their intellectual capacity [19]. So far, there are three reports that are comparable, from Quebec in Canada [19], from Mexico [20] and from Brazil [21], and that give concern regarding the neurotoxicity of manganese in drinking water. A summary of the findings regarding toxicity is published from a conference [22]. Manganese is an essential element and the major intake is via food. Elevated intake via drinking water by women may be positive for foetal survival [23] but foetal growth may be impaired [24]. The intake of manganese via drinking water is smaller but seems unregulated. This is mirrored in hair in which the concentration increases with that in drinking water but not with the intake via food. The Mn²⁺ seems to be taken up by the divalent metal transporter 1 (DMT-1) and be affected by, for instance, iron status [25]. A hypothesis, as humans have not developed a regulation, could be that moderately reduced groundwater from larger depth has, in the history of mankind, not been a common way to get drinking water but rather from surface water and springs.

4. Chromium

Chromium is a genotoxic carcinogen and Cr(VI) is due to its similarity with sulphate taken up by the same pathways. While excess arsenic in groundwater is often a natural phenomenon, the occurrence of chromium is natural as well as anthropogenic. In Greece, a groundwater plume up to 160 µg/l was studied [26]. It was found to be essentially natural but with an anthropogenic component in one area. Chromium is used in stainless steel but major pollution by chromium is from leather tanning and electroplating. Cr(III) forms solid phases in a reducing environment in groundwater but is mobile as Cr(VI) under oxidising conditions. Cr(III) can be oxidised to Cr(VI) by manganese oxides commonly present in soils [27–30].



Kazakis et al. [31] have studied the oxidation of Cr(III) on surfaces of mafic minerals and concluded that it was mediated by manganese oxides. Chromium tends to be present at higher levels not only in ultramafic rocks present in Greece but also elsewhere in the world [32]. Cr(VI) is mobile in groundwater but its mobility is pH dependant, being higher at elevated pH levels depending on the fact that the main adsorbents aluminium and iron oxyhydroxides lose their positive charge at pH above 8 [28]. Soluble organic complexes decrease the oxidation

rate due to complexation with Cr(III) [33]. These authors studied the use of tannery waste for increasing the organic matter content in soils. Cr(VI) may be oxidised to chromate even in an organic matrix like tannery sludge provided the oxygen is high enough [34]. Chromate may then be leached, and it may pollute the groundwater. A number of actions to decrease chromium leaching from leather tanning are proposed [35]. In Punjab, in northwestern India, a sand delta was detected at levels of 5 mg/l at 60 m depth, in this case from electroplating activities [36]. At a level below 2 mg/l in drinking water, chromium can be reduced to Cr(III) which is not taken up by humans.

5. Selenium

Selenium which is an essential metalloid is a part of selenoproteins in the human body. Selenium is ingested via food and drinking water. The concentration varies largely when seen in a global context. The lowest contents are seen in Sweden in the order of 0.1–0.2 µg/l while as high as 480 µg/l are seen [37, 38]. The current guideline is seldom exceeded in drinking water [39]. Nevertheless, these authors demand more studies and especially what concerns specific species of selenium in groundwater. Inorganic species are, as per their results, considerably more toxic than organic species [39]. Selenium deficiency is common in, for instance, Sweden and Finland. In Finland, action has been taken by adding selenium to commercial fertilisers [40]. This selenium is considered to reach humans mainly via the food and the serum-Se has increased while so far no obvious positive health effects are seen in humans but they are seen in animals. However, in Punjab, in northwest India, groundwater concentrations above 300 µg/l have been recorded [41]. In part, the selenium is likely to come from food as groundwater irrigation is common which has caused the accumulation of selenium in cultivated soils. Selenosis in the form of malformed nails is observed [41]. In the area, the main source of selenium is food, contributing about 90% of the total intake [42].

Selenium has a complicated redox pattern with the main species in groundwater being Se(IV) and Se(VI) [1]. Oxidising conditions increased the leaching from soils in the form of Se(VI).

6. Uranium

Uranium is present in rocks in amounts from less than 2 to a few 100 mg/kg. Lowest content is found in ultrabasic rocks while black shales of marine origin can have hundreds of mg/kg [43]. Uranium is well common in granites and is mobile under oxidising conditions. Uranium has a large number of complexes and their mobility depends on their charge, uncharged species being more mobile. Uranium is a risk from both the radiation point of view as well as a chemical risk point of view. It seems that in many cases, the chemical risk is the one that is most important [44, 45]. Its guideline values have been changed repeatedly over the last 13 years and its current provisional guideline is now, what concerns the chemical risk, 30 µg/l [46] (**Table 1**). The chemical risk is its effect on the secondary uptake of water and salts from the primary urine formed in the kidney cortex [45, 47]. The radiological guideline is different for ^{234}U and ^{238}U being, respectively,

Element	Guideline value	Note
Arsenic	10 µg/l	Provisional
Chromium	50 µg/l	Provisional
Manganese	(400 µg/l)	Technical
Nitrate	50 mg/l	
Selenium	40 µg/l	
Uranium	30 µg/l	Provisional

Table 1. Elements exhibiting redox-sensitive behaviour with guideline values. The figures are derived from WHO [5] and regard guidelines due to health reasons. For manganese only a technical guideline is established.

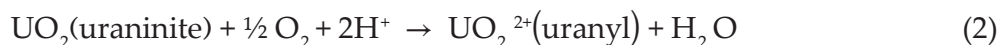
1 and 10 Bq/l [46]. The uptake by humans of different uranium complexes varies considerably. A speciation of uranium complexes can be calculated from an ICP-MS (Induced Coupled Plasma combined with Massspectrometer) analysis by Visual MINTEQ [48] or PHREEQC [49]. Uranium in groundwater is high especially in granitic terrains, for example, in Sweden and Finland. Another source of uranium is in the form of phosphate fertilisers as phosphate rocks have elevated uranium contents [50]. In an area in southern central Finland, the total uranium levels in groundwater were, in some samples, above 3000 µg/l while no health effects were seen [51]. This is far above the current WHO health limit of 15 µg/l. A speciation of the uranium in relatively alkaline groundwater (pH > 7.3) showed that the major portion of uranium was present as calcium-uranyl-carbonato complexes ($\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$). Thus, these complexes do seem to be less toxic or less bioavailable. There seems to be an interaction with the iron status such as the uranium uptake may be higher at iron deficiency [45, 52] which, by these authors, was considered as an action of divalent metal transporter 1 (DMT-1).

Mobility of uranium in groundwater is affected by a large number of factors. In general, U(IV) is less mobile than the oxidised form U(VI) [53]. This is true for several actinides and has been considered in the search for safe repositories for radioactive waste [54]. As mentioned above, uranium forms numerous complexes among them carbonate complexes. Elevated bicarbonate contents in groundwater form soluble carbonate complexes [55]. When removing the uranium ex-situ by filter, for instance, it is important to know the speciation [56].

The reduction of uranium is in part not only inorganic but also bacteriologically mediated by Moon et al. [57]. The microbial reduction results in isotope fractionation [58]. There is a considerable community of bacteria even at hundreds of meters in hard rock terrains [59, 60]. One of the substrates for uranium sequestration could be acetate [53]. Sulphate-reducing conditions are most favourable for the reduction from U(VI) to U(IV) [53, 61]. Species involved in the reduction are *Desulfobacter*, *Desulphoropalus* and *Desulfovibrio spp.* [53]. Oxidation of Fe(II) to Fe(III) can also reduce U(VI) to U(IV) [61].

An example of the redox behaviour of uranium is sandstone-hosted uranium deposits formed by groundwater flow with low concentrations of uranium reaching a redox barrier where the U(VI) is reduced to U(IV) and accumulates as an ore-body. These deposits are now commonly

extracted by in situ recovery with injection of an oxidising solution forming U(VI) and preferably forming an uncharged complex [62]:



Complexation with calcium:



This technology is considerably more environment friendly compared with conventional mining which leaves tailings containing leftover uranium.

7. Nitrogen

Nitrogen is a major nutrient in soils and its cycle has been affected to a large extent by anthropogenic industrial nitrogen fixation, fertiliser production. The nitrogen fixation in nature was passed by the anthropogenic in the 1980s [63]. When organic matter like litter degrades, ammonia is formed. Ammonia is strongly adsorbed on clay minerals and to organic matter, and elevated concentrations are only found close to a point source. Nitrate, on the contrary, is mobile unless it is taken up by plants. While nitrate in surface water may be part of eutrophication, the main risk with nitrate in groundwater is as the formation of methaemoglobinemia and the decrease of the oxygen-carrying capacity of the red blood cells from the lungs to peripheral tissues [64]. This affects children below the age of about 1 year that are bottle fed with high nitrate water. Above the age of 1 year, humans develop an enzyme that recovers the normal haemoglobin. Methaemoglobinemia is not common; a few thousands of cases are reported. Nitrate converted to nitrite in the intestinal tract may be carcinogenic [65]. Nitrate is reduced to nitrite in the intestinal tract and nitrite may form nitrosamines and elevate the risk of gastric cancer [66]. Above all, nitrate in groundwater is a resource in a wrong place; it should be present in the root zone to promote crop growth.

8. Interactions between elements

In a redox reaction, there is an electron donor and an electron acceptor. Among the elements dealt with above, there are interactions. Oxygen is a common electron acceptor under oxidising conditions, for example, the oxidation of As(III) to As(V). Ferric oxyhydroxides play a crucial role for the mobility of arsenic in groundwater in two respects, under reducing conditions, they are dissolved and arsenite is released and under high pH conditions, above pH 8.2, when they are uncharged making arsenate mobile.

Manganese oxides on the surface of mafic minerals [31] and in general in soils [33] can serve as an oxidant of Cr(III), forming mobile chromate.

Selenium is mobile in groundwater under oxidising conditions, and nitrate from agriculture mobilises selenium from marine shales [67]. Another interaction between agriculture and groundwater might be found in rice cultivation. A new rice irrigation practice by using

intermittent irrigation, allowing the rice field to dry up between irrigations, has several positive effects, higher yield, lower arsenic content in the rice grains and lesser methane emission [68]. It might also in the long run affect the groundwater redox conditions.

9. Conclusions

The presence of different species of elements at different redox levels makes assessments of the associated health risks complicated. In addition, the species have different levels of toxicity. A number of trace elements may pose risks to human health, arsenic, manganese, chromium as chromate, nitrate, selenium and uranium. Except for manganese, these species are either uncharged or in the form of anions and their adsorption to soils and aquifer materials is weaker than for cations such as most heavy metals like Cu, Pb and Zn. The main adsorbents for the latter are clay minerals and organic matter, and the adsorption of those increases with pH while the adsorption for anions, by aluminium and ferric oxyhydroxides, decreases with pH and approaches zero, close to ZPC at just above pH 8. Uncharged species are particularly mobile like arsenite.

Arsenic is mobilised into groundwater both under reducing and oxidising conditions. With reduction of ferric oxyhydroxides, ferrous iron and arsenite are released into groundwater. This is common especially in south and southeast Asian delta regions. While removal by filter is possible, but not always functioning due to social reasons and in addition gives a waste problem, an alternate way of supplying safe water is to identify aquifers with more oxidising environments. This can be done by examining the colour of the sediments. White, off-white and red sediments are likely to yield a low arsenic groundwater. It is also possible by the colour code to identify low manganese groundwater. In oxidising environments at neutral pH, arsenate (As(V)) is immobilised into ferric hydroxides. However, at pH above 8, these adsorbents lose their positive charge and arsenic becomes mobile.

Chromium is carcinogenic and mobile in oxidising environments. Chromium comes from both natural and anthropogenic sources. Ultramafic rocks are high in chromium. Main anthropogenic sources are electroplating and leather tanning. Manganese oxides in soils and on mafic minerals can act as oxidants of Cr(III) to form mobile chromate (Cr(VI)).

Selenium, an essential element, seldom reaches toxic levels in groundwater, but in areas where irrigation is practised with groundwater, with elevated selenium concentrations, the intake via the crops cultivated can be too high. Nitrate may act as the oxidant of Se(IV) and form mobile Se(VI).

The nitrogen cycle has been radically changed by human action mainly through the industrial production and use of nitrogenous fertilisers. The natural symbiotic nitrogen fixation was exceeded by the anthropogenic in the 1980s. Nitrate or rather nitrite formed in the human intestinal tracts could be carcinogenic by forming nitrosamines. However, the main reason for the guideline value at 50 mg/l is the risk of methaemoglobinemia in bottle-fed children below the age of 1 year. Breastfeeding efficiently counteracts this.

Uranium can be toxic from radiological point of view but more often due to its chemical action on the re-adsorption of water and salts from the primary urine formed in the kidney cortex. Uranium speciation is important both for its mobility and for its toxicity. Uncharged species are mobile. Calcium-carbonate complexes do not seem to be taken up by humans. U(IV) is largely immobilised while U(VI) is mobile. In the search for safe repositories for radioactive waste, reducing environments are preferred. These immobilise many other radioactive elements.

Author details

Gunnar Jacks

Address all correspondence to: gunnjack@kth.se

Division of Land and Water Resources, KTH Royal Institute of Technology, Stockholm, Sweden

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