Natural radionuclides in groundwater as pollutants and as useful tracers

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ABSTRACT: Natural radionuclides of the uranium and thorium series are present at mBq/l concentrations up to some Bq/l in many aquifers worldwide. Health impact from these radionuclides when present in drinking water results from ingestion, inhalation of outgassing radon and from possible radionuclide accumulation when water is treated. Activity retained in filters may lead to increased dose rates and contamination problems at workplaces. An example for this frequently neglected exposition path is shown. Uranium and thorium series radionuclides' omnipresence make them attractive free tracers. Mainly disequilibria in the series tell a great deal about geochemical and transport processes. We show how radium/uranium/radon correlations in thermal springs can be used to study mixing processes. Most of the natural radionuclides found in groundwater and worth analyzing either for their health impact or their use as natural tracers are alpha particle emitters. Traditional radiochemical methods to determine alpha emitters are very time consuming and use toxic or radioactive chemicals. We thus are using a simple preparation method for alpha spectrometry that produces no toxic waste and needs no sophisticated lab infrastructure.

1 INTRODUCTION

Radionuclides of the uranium and thorium series are isotopes of 8 different elements from thallium up to uranium. Their half-lives cover more than 12 orders of magnitude. In groundwaters having drinking water quality fortunately few of these elements are soluble, mainly uranium, radium and radon. Half-lives and redox conditions further restrict the number of radionuclides found at concentrations above 10 mBq/l in springs or wells. Under reducing conditions radium remains in solution, but uranium tends to precipitate. Under oxidizing conditions iron- and manganese-hydroxides can form, adsorbing radium efficiently, whereas uranium stays soluble, particularly when complexed by carbon dioxide. Redox conditions have no influence on radon's solubility, but decay of radium adsorbed on hydroxides may lead to locally high radon concentrations. Radionuclides worth analyzing, either because of their health impact or their potential use as natural tracers thus are ^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra and ^{222}Rn.

2 EXPERIMENTAL

^{238}U, ^{234}U and ^{226}Ra are determined by alpha spectrometry using a simple preparation method that avoids toxic chemicals, needs no sophisticated

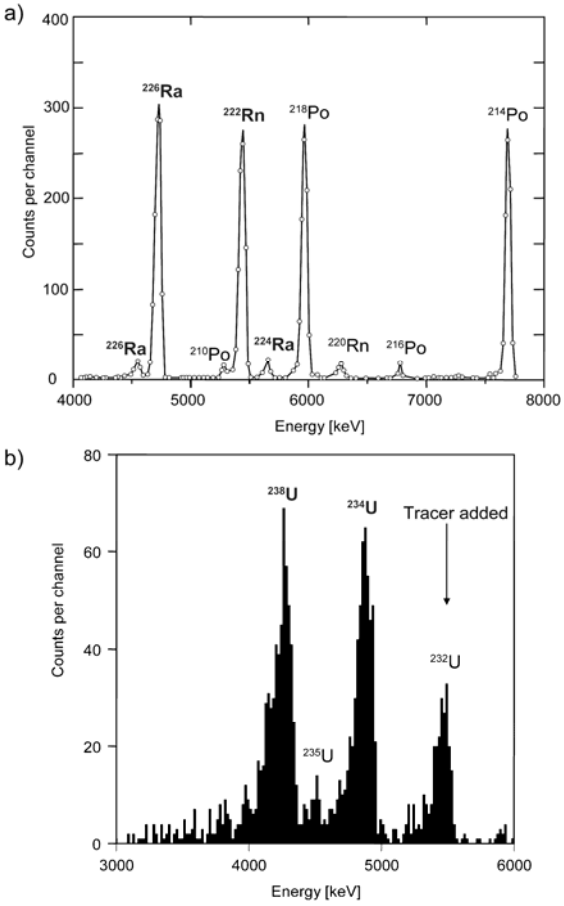

Fig. 1: a) Mineral water "Pedras Salgadas" (Portugal), approx 1500 mBq/l ^{226}Ra b) mineral water "Aproz Ancienne" (Switzerland), approx. 500 mBq/l. Both spectra measured with a 900 mm^2 Si alpha detector for 80'000 s.

lab infrastructure and leaves no toxic or radioactive wastes (Surbeck 1995; Surbeck 2000). Recent tests have shown the formerly used formic acid can be replaced by citric acid, a food additive. The preparation method is based on the selective adsorption on thin films. Detection limits for the three isotopes are 5 mBq/l for a 100 ml sample. Typical spectra are shown in figure 1. ^{228}Ra, a beta/gamma emitter is adsorbed together with ^{226}Ra on the thin films and can be determined by a second alpha measurement after a partial buildup of ^{228}Th (Eikenberg et al. 2001)) ^{222}Rn batch samples are measured by liquid scintillation counting. Detection limit for a 10 ml sample is below 0.5 Bq/l. A well-type HP-Ge detector is used to determine gamma emitters in solid samples.

3 RESULTS AND DISCUSSION

3.1 Health impact from radionuclides retained in water filters

Because of its high dissolved iron content a mineral water from a spring in eastern Switzerland needs treatment before it can be bottled and sold. Aeration of the water leads to iron hydroxide precipitation. This iron hydroxide is then retained in a large quartz sand tank. This efficiently reduces the iron concentration but creates a new problem. A considerable part of the radium dissolved in the groundwater is adsorbed on the iron hydroxide. As the radium concentrations in the water are quite high this leads to an accumulation of large radium activities in the filter. Backwashing only removes a small part of the activity. After some months operation, activities of several kBq/kg have been found in filter sand samples (Fig.2). At the filter tank surface, gamma dose rates of several 100 nSv/h can be measured.

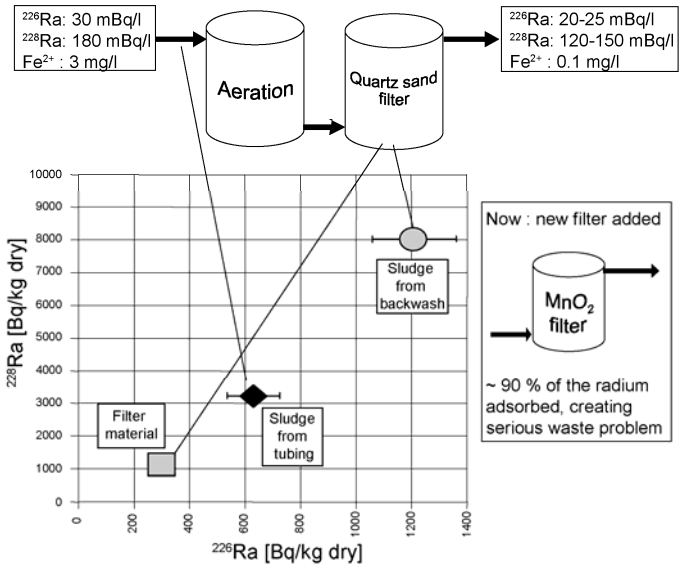

Fig. 2: Radium accumulation in filters and sludges at a Swiss mineral water bottling plant.

In addition iron hydroxide sludge accumulates in the tubing and has to be removed from time to time. Together with the backwash water from the filter this highly active material is regularly flushed into the nearby river .The increased dose rate close to the tank is not really a health problem for there is no permanently occupied working place close to. However there could be serious contamination problems when handling the high activity filter material and sludges. In addition, actually nobody knows how to get rid of all this "radioactive waste". It should neither end up in the river where it could enter the food chain, nor in an ordinary waste dump where it could put workers there at risk or contaminate the groundwater. Recently thing have even turned worse. An additional filter has been installed to remove traces of manganese. This manganese-oxide filter retains essentially all radium. This may be an extreme case, but similar problems may arise at many water treatment plants. Some 10 mBq/l of radium dissolved in the water to be treated is all you need to produce kBq/kg in the filter material and in the sludge.

3.2 Uranium series radionuclides as natural tracers

In order to look for possible correlations, we have sampled springs and wells with known thermal anomalies at several sites in Switzerland (Alps: Saxon, Bad Ragaz, Leukerbad, Val d'Illiez, Combioula, Brigerbad and Leytron, Jura Mountains: Yverdon, Moiry and Delémont). Most sites are in sedimentary rocks, resulting in Ca-HCO_3 and Ca-SO_4 water types. Waters of Combioula and Lavey discharge from crystalline rocks.

As can be seen in Figure 3, there is a positive correlation between the temperature and the **radium** concentration. As radium is more mobile in reducing environments (Ames et al. 1983; Banks et al. 1995; Langmuir & Riese 1985; Szabo & Zapecza 1991), we expect higher radium concentration in anoxic deep thermal water. Figure 3b shows that radium is mostly below detection limit in highly oxygenated water while it can be relatively high in warm anoxic water. Radium adsorption on iron-hydroxides not only happens in filter as described above, but also in natural systems (Bamberger 1914; Gainon et al. Accepted; Schott & Wiegand 2003). When anoxic deep thermal waters get mixed with near-surface cold and oxygen rich waters iron-hydroxides may precipitate. Adsorption on these iron-hydroxides removes some of the radium. This radium, sitting close to the surface is then producing radon that can easily escape to the water phase. For waters rising up from the same deep aquifer but undergoing different mixing with cold near-surface waters, we thus expect a negative correlation between the radium concentration and

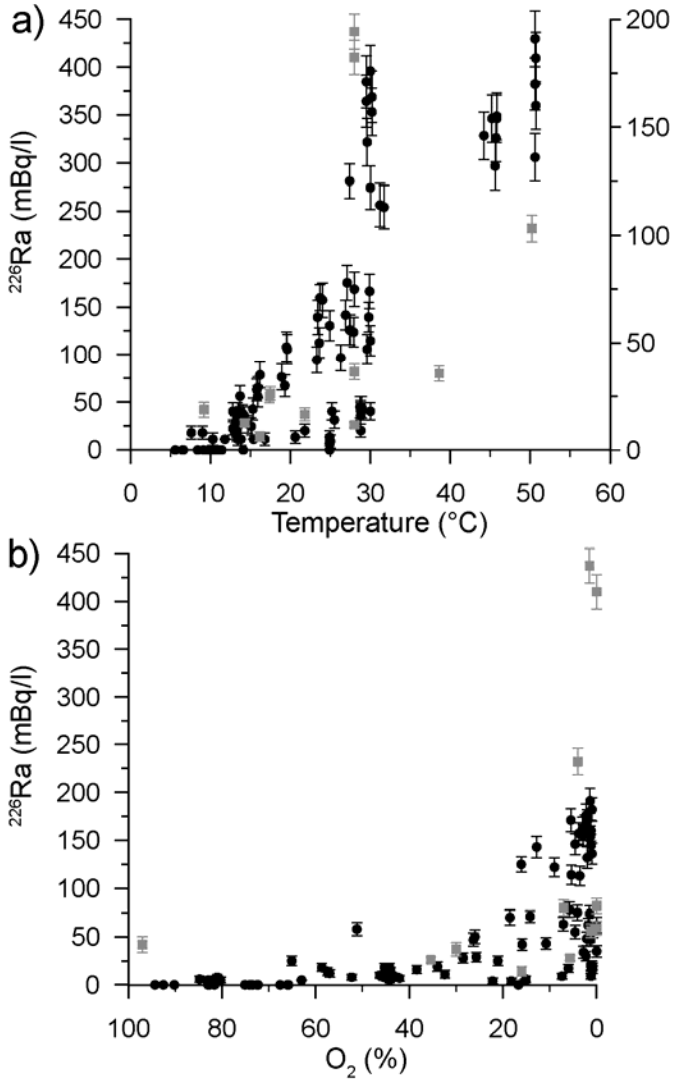

Fig. 3: ^{226}Ra content in Swiss thermal waters. Black circles represent water from carbonate rocks and evaporites (graph a: right y scale), grey squares represent water from crystalline rocks (graph a: left y scale).

the radon concentration. When looking at radium vs. radon for different springs at the same site (fig. 4), there is a negative correlation between radium and radon.

Radium lost by adsorption on iron-hydroxides efficiently produces radon. Plotting the **radon/radium ratio** vs. temperature seems to be particularly helpful to estimate mixing ratios. The lower the ratio, the less deep water has been mixed with shallow oxygenated water. This is well illustrated by the data for the test site Yverdon, in particular for the thermal spa. The well is at a distance of only 20 m from the old spring and goes to a depth of 500 m. Both waters thus probably have the same initial composition deep down. During uprising, the spring water mixes with shallow water, resulting in iron hydroxide precipitation, radium adsorption and radon production. This explains why the ^{222}Rn/^{226}Ra ratio for the old spring is higher than for the well water (Fig. 5)

Contrary to radium, **uranium** is more mobile under oxidizing conditions, forming the soluble UO_2^{2+}. In

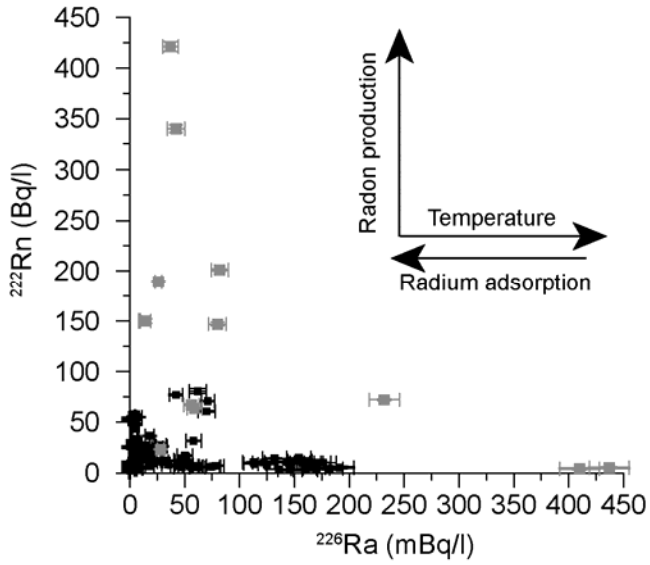

Fig. 4: ^{226}Ra vs. ^{222}Rn in Swiss thermal waters. Black circles represent water from carbonate rocks and evaporites, grey squares represent water from crystalline rocks.

its reduced form (U^{4+}) it is quite insoluble (Albu et al. 1997; Herczeg et al. 1988; Szabo & Zapecza 1991). Therefore we expect lower uranium concentrations in hot anoxic water than in water cooled down by mixing with oxygenated cold water. As can be seen in Figure 6, uranium contents in fact tend to decrease with increasing water temperature.

The uranium concentrations in water from crystalline rocks are generally higher, under the same redox and temperature conditions, than concentrations in water from sedimentary rocks. Uranium content of the water of Saxon (zone a in figure 6) is a special case. Although this water is of the carbonate calcite type, its uranium content fits better with water from crystalline rocks and, thus has been plotted with the latter. A part of Saxon water probably originates from crystalline rocks.

4 CONCLUSION

Iron and manganese hydroxides play a crucial role in the radioisotope speciation in groundwater, even at low concentrations of dissolved iron or manganese. The resulting disequilibrium in the uranium decay series may give information on a regional hydrogeological system, as mainly radium/radon ratios have shown. Naturally present radioisotopes may thus be a usefool additional tracer.

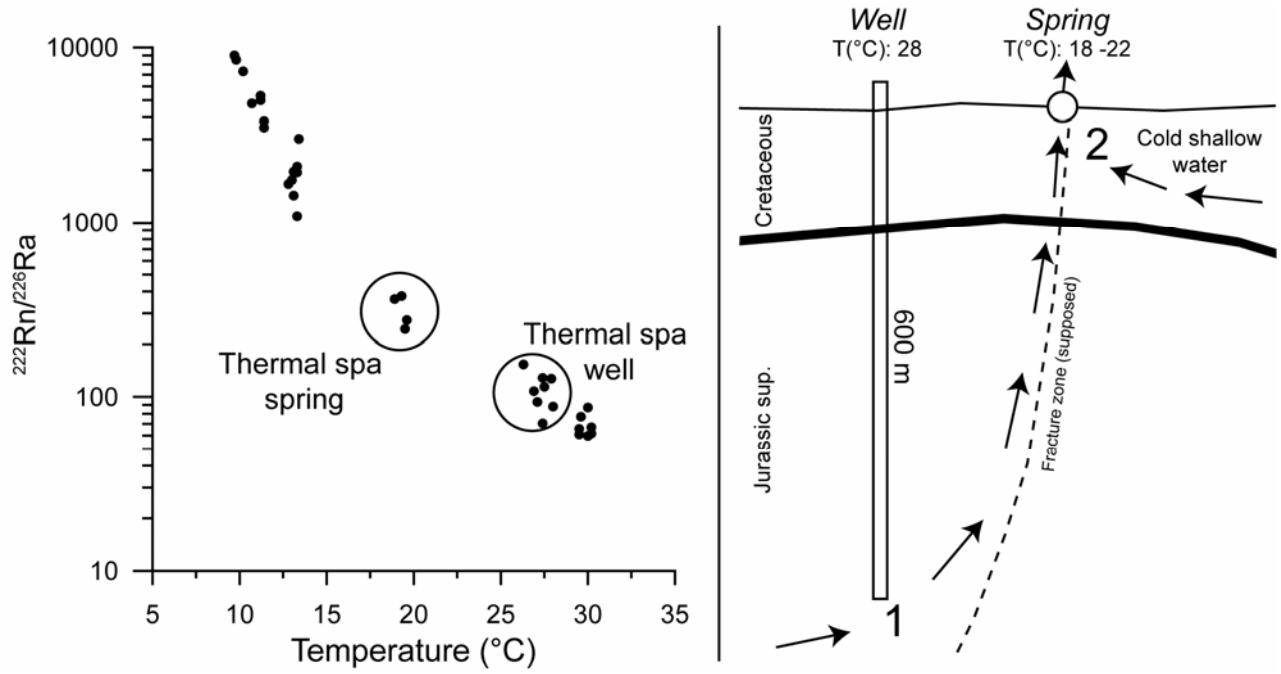

Fig. 5: $^{222}Rn/^{226}Ra$ ratio in the water of the Yverdon test site and sketch of the pathway of thermal spa water. Zone 1: reduced water with low $^{222}Rn/^{226}Ra$ ratio. Zone 2: mixing between thermal water and cold shallow water: iron hydroxide precipitation, radium adsorption and radon production => increase of the $^{222}Rn/^{226}Ra$ ratio.

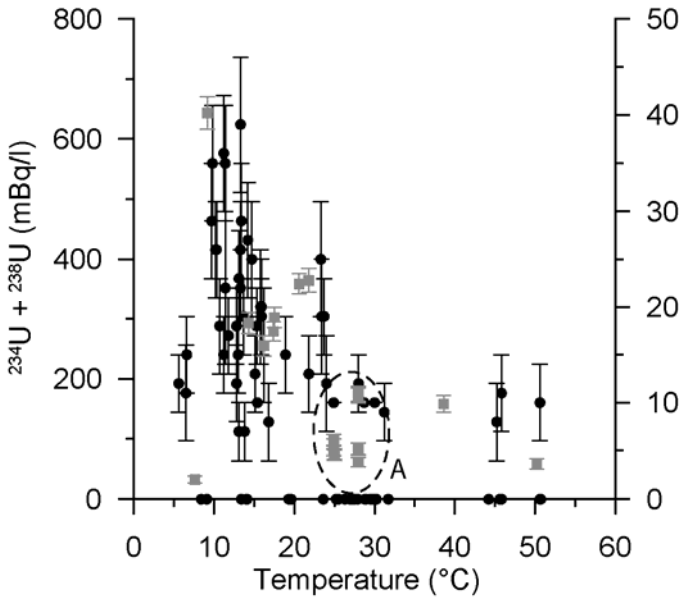

Fig. 6: $^{234}U + ^{238}U$ content in Swiss thermal waters. Black circles represent water from carbonate rocks and evaporates (right y scale), grey squares represent water from crystalline rocks (left y scale). Grey squares of zone A: Saxon water

AKNOWLEDGEMENTS

We would like to thank the City of Yverdon and the Swiss Federal Office of Public Health for their financial support.

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