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Spatial and temporal variations in the uranium series background in Alpine groundwater

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Abstract. In areas with uranium mining it is hard if not impossible to decide if increased uranium, radium or radon levels are due to these industrial activities or if they are just natural variations. There are rarely reliable data available taken prior to mining. Therefore our data from the Swiss Alps, a region with known uranium mineralizations but no uranium mining may help to get an idea about the range of spatial and temporal variations of the natural background. They may also serve as a baseline against which possible influences of climate change or future industrial activities in the Alps can be compared.

Introduction

A search for uranium mineralizations in Switzerland started around 1950 (Payot 1953) with the measurement of ^{222}Rn and ^{226}Ra in numerous Swiss springs, neglecting the already then known fact that temporal variations can mask spatial ^{222}Rn variations (Perret 1918) and that radium is a bad proxy for uranium because of it's very different geochemical behavior. The study thus did not give any useful hint where to look for uranium. More successful have been dose rate measurements above ground and in tunnels excavated for the then fast developing Alpine hydroelectric plants (Gilliéron 1988). However, as is the case for most minerals in the Swiss Alps, ore deposits turned out to be frequent but too small to be mined commercially. Some tons of uranium rich ore from the only exploration tunnel ever dug were sold to France and some hundred kg finished in university collections.

There have been small coal, lead, copper, gold and iron mines in the Swiss Alps, some with increased uranium concentrations (Woodtli et al. 1987), but none

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has been a lasting commercial success. They have never been productive enough to lead to important tailings.

The largest tailings ever seen in the Swiss Alps are currently building up. They are the result of the ongoing excavation of two large railway tunnels, both together more than 80 km long. Systematic and at some places continuous dose rate measurements of the extracted material showed that no important uranium ore deposit has been hit so far .

To summarize, there are numerous small uranium anomalies in the Swiss Alps, but there has been no important mining activity that could have led to considerable groundwater contamination. We thus consider the Swiss Alps as a favorable area to study natural variations in the uranium series concentrations in groundwater.

The work presented is the result of several studies carried out between 1995 and 2005 (Deflorin and Surbeck 2002, Deflorin 2004, Gainon 2003, Kloos 2004 and unpublished internal reports of the Swiss Federal Office of Public Health) in the

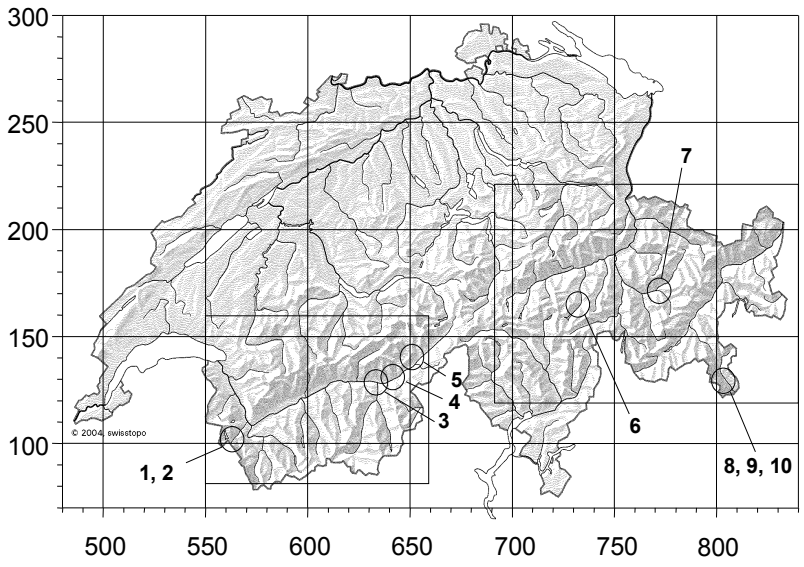

Fig. 1 : Swiss map with the study areas outlined. Circles show the sites of the springs (Nr. 6 to Nr. 10) and public fountains (Nr. 1 to Nr. 5) where time series have been taken. 1: Châtelard Frontière, 2 : Finhaut, 3 : Visp, 4 : Brigerbad-Dorf, 5 : Lax, 6 : Vals Leis, 7 : Bergün, 8 : Poschiavo Pedecosta, 9 : Poschiavo Al Bait, 10 : Poschiavo Sass da Li Rondolli. Coordinates given are the Swiss National N-S/W-E km coordinates.

Cantons of Grisons (eastern part of the Swiss Alps) and Valais (western part of the Swiss Alps). The two areas covered are shown in Fig.1. We consider the large spatial and temporal variations observed for uranium, radium and radon concentrations in groundwater as being representative for a young mountain range with complex geologic and tectonic features. We have no intention to propose our data as

beeping representative for mature old ranges like the Erzgebirge, but they show clearly how large variations can be, even without industrial impact. Our data may also serve as a baseline against which possible impacts of climate change or future industrial activities in the Alps can be compared.

We are well aware of the fact that even dense spatial and temporal sampling will never cover all possible variations. We thus also present what we think we have learned from these data about processes leading to these large variations.

Only uranium series data are shown here, although ^{228}Ra has also been measured for all Canton of Grisons samples (for these additional data see Deflorin 2004, for the analytical method used Eikenberg et al. 2001).

Experimental

All samples have been taken either by cantonal drinking water inspectors, by hydrogeologists or by scientific personnel with a good knowledge in water sampling. Depending on the measurement technique used, 10 to 250 ml samples were taken in glass bottles for the radon determination and approx. 250 ml (unfiltered, not acidified, PE- or PET-bottles) for uranium and radium determination. Samples have been taken as close as possible to the springs or in the case of pumped groundwater as close as possible to the pumps, after sufficient pumping time to have a representative sample. A total of approx. 400 different springs and groundwaters have been sampled in the Canton of Grisons and approx. 50 in the Canton of Valais. Samples in the Canton of Grisons cover all public drinking water supplies and all known mineral water springs. Sampling in the Canton of Valais has been more biased towards springs that seemed to be interesting from a geological point of view. For 5 springs and 5 public fountains (locations see Fig.1) time series where taken over periods from months to several years, in general a sample a month.

Uranium has either been determined by ICP-MS or by alpha spectrometry (Surbeck 2000). ICP-MS data have been converted to ^{238}U activity by applying a factor of 12.4 mBq/l per ppb U. All ^{226}Ra determinations have been made by alpha spectrometry (Surbeck 2000). For ^{222}Rn either bubbling in a closed circuit (measurement in the gas phase with a RAD7 (Niton)) or liquid scintillation counting after liquid-liquid extraction (extraction with MaxiLight (Hidex), measurement with Tricarb (Canberra Packard) or Triathler (Hidex)) has been used. For measurement uncertainties see error bars in Fig. 4.

Results and Discussion

Figure 2 shows the spatial distributions for ^{238}U, ^{226}Ra and ^{222}Rn on a 50 km grid and Fig. 3 zoomed parts at 10 km and 1 km grid sizes. They show how large spatial frequencies can be. Cumulative frequencies for the Canton of Grisons data can

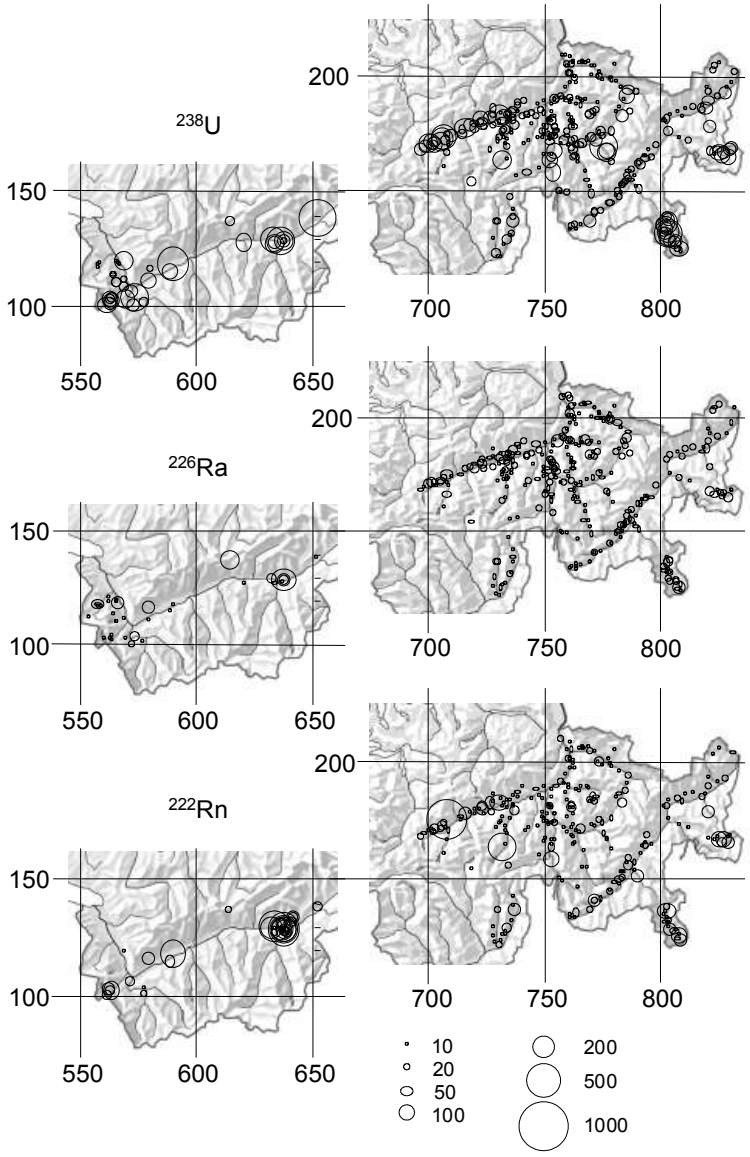

Fig. 2 : Spatial distribution for ^{238}U, ^{226}Ra and ^{222}Rn. Units for ^{238}U and ^{226}Ra are in mBq/l, for ^{222}Rn in Bq/l. For measuring uncertainities see Fig.4. Coordinates given are the Swiss National N-S/W-E km coordinates.

be seen in Fig. 4. At low concentrations not all the points are drawn. Up to a cumulative frequency of 80 % every 10th value is drawn, from 80 % to 90 % every 5th, from 90 % to 95 % every second. All values are drawn above a cumulative

frequency of 95 %. Data for drinking water and data for mineral water springs are drawn separately.

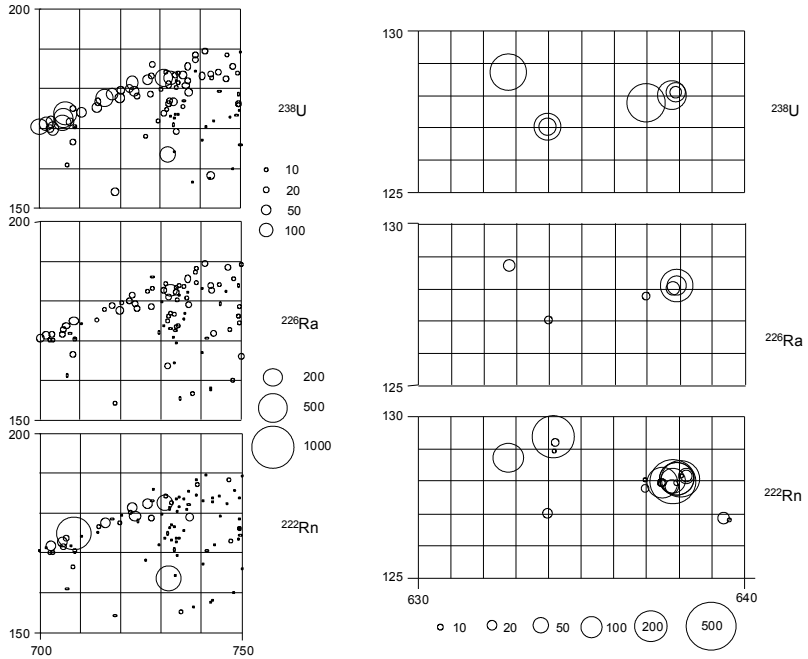

Fig. 3 : Zoomed parts of Fig.2, showing high spatial frequencies.Units for ^{238}U and ^{226}Ra are in mBq/l, for ^{222}Rn in Bq/l. For measuring uncertainities see Fig.4.

No cumulative frequencies for the Canton of Valais data are presented because of the potential sampling bias mentioned above.

Cumulative frequencies clearly show lognormal distributions. Uranium and radon frequency distribution are very similar for drinking water samples and mineral water samples respectively. However for ^{226}Ra the two distributions are clearly different. This behavior may be due to the fact that waters with low oxygen concentrations are not used as drinking water whereas mineral waters in general are anoxic. In anoxic groundwater there is no iron-hydroxide precipitation and thus dissolved radium is not adsorbed. Large sampling campaigns like the one we did in the Canton of Grisons, with a total of more than 400 samples, take some time. In our case three months from March 2002 until May 2002. During this period precipitations have been frequent but irregular and snowmelt at higher altitudes had just started. We thus can't be sure that we did not mix up spatial and temporal variations. To get an idea how large temporal variations can be we sampled 5 springs in the Canton of Grisons and 5 public fountains in the Canton of Valais monthly for a whole year. Figure 5 shows the uranium data for these samples. Variations are considerable even for the 5 Grisons springs where anthropogenic influences can be excluded. The extreme variations for one of the the public fountains

(Brigerbad-Dorf) turned out to be an intentional mixing, due to a drought, with water from a nearby village. Claimed origins of fountain waters may sometimes just be wishful thinking.

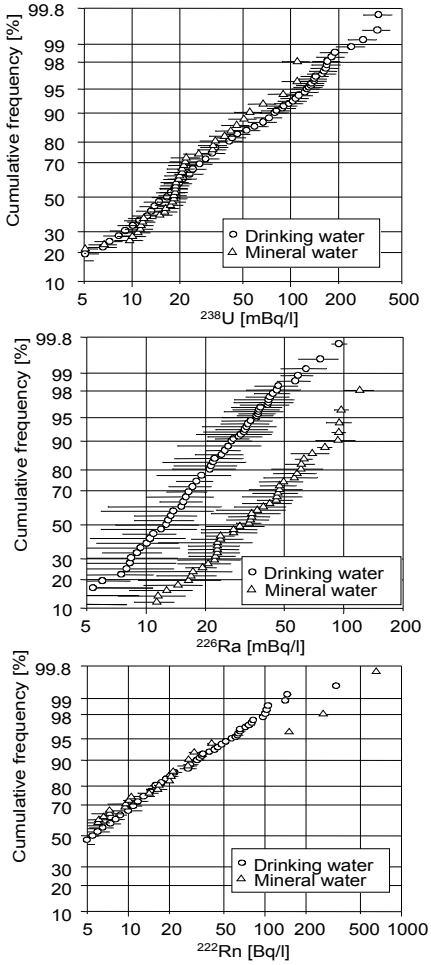

Fig 4 : Frequency distributions for the Canton of Grisons data. Drinking water : 360 samples, mineral waters : 42 samples. Error bars correspond to 1 sigma counting statistics for ^{226}Ra and ^{222}Rn and to a total uncertainity of 20 % for the ICP-MS uranium data.

We assume that monthly sampling has been adequate for the type of springs considered. However we are well aware of the fact that a better temporal resolution may bring to light even larger variations, for example in Karst springs (Eisenlohr and Surbeck 1995, Savoy and Surbeck 2003, Bossy and Surbeck 2004).

Sampling in the Canton of Grisons has been very dense, but it is impossible to sample every spring or well in the whole Swiss Alps. As the time series show it would even be necessary to take samples at least once a month.

Therefore some ideas about the geochemical processes behind are needed for a more targeted search. First steps to a conceptual model are the following trends we have seen in our data : 1) radon concentrations above 50 Bq/l are very local phe-

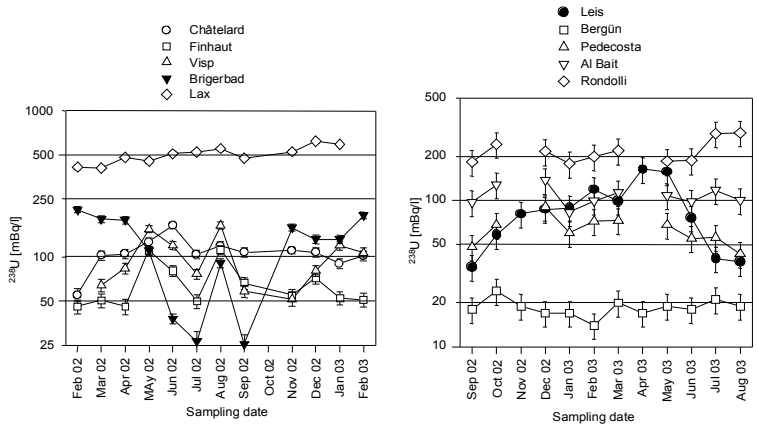

Fig. 5 : Uranium **t**ime series for the 5 springs and 5 public fountains marked in Fig.1.

nomena, connected to radium adsorptions on iron hydroxides produced by the mixing of oxygen rich young waters with old anoxic waters (Gainon 2003), 2) anoxic waters from limestone formations generally show increased ^{226}Ra concentrations (up to 200 mBq/l). The higher the temperature the higher the ^{226}Ra concentration (Kloos 2004), 3) increased uranium concentrations (> 100 mBq/l ^{238}U) are found in a) cold, oxygen rich, low mineralized waters from crystalline rocks with at least part of the uranium present as UO_2^{2+} and b) cold, highly mineralized (mainly sulfate) waters with no significant sign of UO_2^{2+}, but strong evidence for complexation with CO_2.

Conclusions

Large spatial and temporal variations in the uranium series concentrations have been observed in groundwaters in an area rich in poor uranium ore deposits, but without any important mining activity. Our data are for a young mountain range, but may also be of some help to assess claims about the impact of mining activities elsewhere. In addition these data can be used as a baseline against which impacts of climate change or future industrial activities in the Alps can be compared. Temporal variations turned out to be important, masking or simulating at least some spatial variations. First trends observed in our monitoring data open the way to a conceptual model for a more targeted sampling.

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