Dissolved gases as natural tracers in karst hydrogeology; radon and beyond

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Abstract. Gases present in the atmosphere or produced in the soil dissolve in rainwater and then are transported by percolation down to the saturated zone. Of particular interest are gases like radon and CO_2 that have a well delimited place of production and that can be measured continuously in the field. Both are mainly produced in the soil, but have different chemical and physical properties. Radon decays with a half live of about 4 days whereas CO_2 reacts with the carbonate on its way down to the saturated zone. Temporal variations of their concentrations in underground rivers or in spring water can thus be used to gain information about fast transport processes in karst systems. Other dissolved gases, mainly oxygen and nitrogen may show short peaks of supersaturation due to a clogging of parts of the conduits in the vadose zone during high flow. Still not well known among hydrogeologists, supersaturation, that can be easily measured continuously in the field, may become a useful tool to study dynamics in karst systems. This lecture has mainly the intention to make you familiar with radon, CO_2 and TDGP measurements and to show what they can be used for. It's not so much about well established techniques and contains some unproven claims and open questions.

Introduction

Gases present in the atmosphere can dissolve in rainwater and thus be transported down to an aquifer. Other gases are produced in the soil and are taken up by percolating water. Comparing the concentrations of all these gases in underground rivers

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or at springs with the concentrations in rainwater or in the soil can give valuable information about transport processes in a karst system. Dissolved gases can thus serve as natural tracers. Naturally present tracers have the advantage that they are free and abundant. However their omnipresence is also a disadvantage. There may be distributed, not well localized sources.

At least for two gases, radon and CO_2, this is less a problem in soil covered karst. Radon production in the soil is far larger than in even heavily fractured limestone and outside air radon concentrations are orders of magnitude below soil gas radon concentrations. CO_2 is also mainly produced in the soil and leads to soil gas CO_2 concentrations at least 10 times as high as in the atmosphere. In some cases there may be a CO_2 contribution from deep down. Radon from deep down is not very probable because of its short half-live of less than 4 days. We thus have two gases with the same, well localized production place but with different physical and chemical properties.

Although deep radon origin is not probable there are cases where radon levels in springs are by far too high to be due to soil radon. These springs, frequently subthermal or thermal may get their radon from radium adsorbed on shallow iron hydroxide deposits that have formed by the interaction of deep anoxic waters with young karst water rich in oxygen.

Rare gases other than radon, He, Ne, Ar, Kr and Xe are, with the exception of Ar, that makes about 1%Vol in outside air, only present at trace levels in the atmosphere and are less soluble than radon. However, it's a well established, although expensive technique to use the concentration ratios of these rare gases to determine infiltration temperatures. Some radioactive rare gas isotopes other than radon can help to date groundwaters, but their half-lives are by far too large to be useful to study karst systems.

Methane produced in the soil, in sinkholes or caves by the decomposition of organic material could be interesting, but methane's water solubility is very low.

Oxygen and nitrogen are the dominant components in outside air and are well soluble. They contribute most to the total pressure of dissolved gases (TDGP, sum of the partial pressures of the individual gases). If TDGP is larger than the atmospheric pressure we have supersaturation. Supersaturation is called “excess air” in the above mentioned rare gas studies. It is considered a nuisance, complicating rare gas data interpretation. Supersaturation is well known and well studied in diving and fish farms. If TDGP exceeds atmospheric pressure plus hydrostatic pressure bubbles can form, harming or even killing divers or fish.

Supersaturation is not well know among hydrogeologists although it may contain valuable information about karst dynamics. We have observed sharp peaks during high flow at a karst spring in the Swiss Alps, probably due to the compression of air pockets. As our studies show supersaturation in karst springs is rather the rule than the exception.

Transport processes in karst systems cover a large temporal range, from below hours to years. Monthly or even daily sampling frequently misses the point. Most valuable are thus continuous measurements with a temporal resolution on the order of an hour. As will be shown this is no problem for radon, CO_2, methane and with new optical sensors also for oxygen. Another gas parameter easily measured continuously is the TDGP.

The last chapter is about how high radon concentrations may be produced. It is less about karst for up to now we did not measure really high radon concentrations (> 50 Bq/l) in Swiss karst springs. This may be different in other countries, at least in Hungary there are karst springs with up to some 100 Bq/l. Although there is still a firm believe in a deep origin of this radon, I'd like to present an alternative, a model supported by data from Switzerland.

This lecture has mainly the intention to make you familiar with radon, CO_2 and TDGP measurements and to show what they can be used for. It's not so much about well established techniques and contains some unproven claims and open questions. It's up to you to test these ideas and to go on.

What gases and where they are from

Outside air composition is dominated by oxygen(21 vol%) and nitrogen(78 vol%). Carbon dioxide amounts to about 0.04 vol%. Rare gases He, Ne Ar, Kr, Xe and Rn are, with the exception of Ar, that makes nearly 1 vol%, only present at trace levels. Other rare gases than radon will not be discussed further. There already exists an extensive literature about their use as natural tracers in earth sciences. Rn is produced by the radioactive decay of Ra found in rocks and soils. It diffuses out to the atmosphere. At several meters above ground the only radon isotope found is ^{222}Rn ($T_{1/2}$ = 3.8 days), the daughter product of ^{226}Ra. The other radon isotopes (^{220}Rn, $T_{1/2}$ = 5 min. and ^{219}Rn, $T_{1/2}$ = 4 s) are too short lived to have survived. Typical ^{222}Rn concentrations at several meters above ground are 10 Bq/m^3 (1 Bq = 1 disintegration / s).

Gases present in the atmosphere can dissolve in rainwater and eventually reach the aquifer.

Gases prominently produced in the soil are carbon dioxide and radon. CO_2 has its origin in bacterial activity and release from plant roots. Both processes depend on the temperature and on climate conditions in general. Soil gas CO_2 concentrations thus show diurnal as well as seasonal variations. Typical CO_2 soil gas concentrations are on the order of 1 vol%. In some rather rare cases there may be a contribution from deep down. Soil gas measurements carried out in the Lower Engadin (Switzerland) show both components (Majoraz 2004).

Radon in soil gas has its origin in the radioactive decay of radium present in the soil. - In the text below radon always means ^{222}Rn and radium means ^{226}Ra -. Depending on where the radium sits, a variable fraction of the radon produced can escape to the pore space and thus be available for transport. Only radon produced very close to the grain surface, within less than a fraction of a micrometer, will be able to reach pore space. Even high radium concentrations in the bulk of heavy mineral grains will thus not lead to high radon concentrations in the pore space. On the other hand, low to moderate radium concentrations will lead to high radon concentrations if the radium is present adsorbed on the surface of the grains. This is frequently the case in well developed soils, where dissolution and adsorption processes have lead to secondary radium accumulation on the surface of soil grains. Iron- and manganese-oxyhydroxides play a major role in these adsorption processes for they are excellent radium scavengers. The fraction of the radon produced available for transport (emanation coefficient) varies between less than 10 % for sandy or gravelly soils to over 70 % for some soils in the Swiss Jura Mountains. In typical Swiss Plateau soils 20% of the radon produced is available for transport. Soil gas radon concentrations at a depth of > 50 cm vary between some 100 Bq/m^3 and several 100 kBq/m^3. Most values in Swiss soils are on the order of 10 kBq/m^3. Radon present in soil gas will be dissolved in the percolating water and carried down to the aquifer (Surbeck & Medici 1991b). Figure 1 shows what radon concentrations in soil pore water are to be expected. The bottom line corresponds to a clean gravel or fractured rock with no surface deposits. The top line is for the extreme case where all radium activity is found at the surface, e.g. adsorbed to iron- or manganese-hydroxides, an excellent scavenger for radium. Values above about 20 Bq/l are only possible if there is a radium enrichment at the surface.

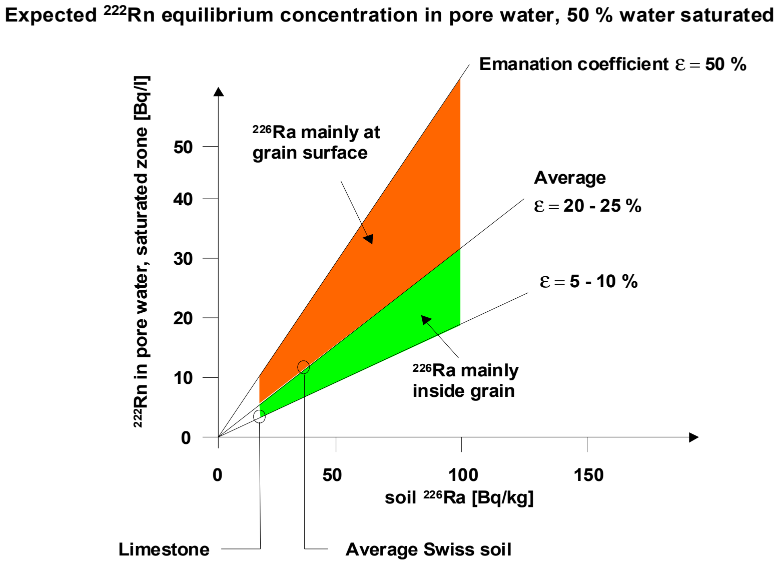

Fig.1: *Expected ^{222}Rn concentrations in pore water vs. soil ^{226}Ra concentration for various emanation coefficients.*

Soils in the Swiss Jura Mountains frequently show not only extremely high radium concentrations, but also very high emanation coefficients. This "anomaly" is probably due to a fast, plant assisted limestone dissolution and an accumulation on small abundant very porous granules composed of clay minerals, iron- and manganese-oxyhydroxides and organic material (Gaiffe 1987, Surbeck 1991a., Von Gunten et al. 1996). It would be worth to look for similar natural radium "anomalies" in other parts of the world. Soils covering karst terrains in moderate humid climate would be good candidates.

There is not much known about radon production in the epikarst, the interface between soil and karst. Our very limited data from the Swiss Jura Mountains show a sharp decrease in soil gas radon concentration below the soil, where epikarst starts. Cave deposits seem not to be an important radon source, however there are only very limited data available.

Limestone is a bad radon source. Low radium concentrations, about 10 Bq/kg in Swiss Jura Mountain samples, with the radium present in the bulk, not at the surface, not only mean a low production but also a very low emanation coefficient. In addition even a heavily fractured limestone is still far less "fractured" than a soil.

Radon from deep down is not very probable. At least in the Swiss Jura Mountains there is no candidate for high production down there and the short half-live of only 4 days would limit its contribution considerably. Until now we have had no case where radon concentrations in karst caves or karst waters would not be well explained by soil radon. There is simply no need for radon from deep down.

Methane produced in the soil, in sinkholes or caves by the decomposition of organic material could be of some interest as natural tracer. It is only present at trace amounts in the atmosphere, but few data about natural degradation in karst systems are available and its water solubility is very low. However one should keep an eye on methane. It is easily measured in the field.

Physical and chemical behavior

Oxygen, nitrogen and carbon dioxide are all well water soluble. Whereas N_2 is chemically very stable, oxygen may be used up in the presence of organic material. Dissolved carbon dioxide reacts with limestone. The concentration of free CO_2 in the water will thus decrease on its way from the soil through the limestone down to the aquifer. In caves, the CO_2 partial pressure is in general lower than in the percolating water. Outgassing then leaves to calcite precipitation, to the formation of stalactites and stalagmites.

Among the rare gases Rn is the most water soluble (Gockel 1914, Clever 1985). No compounds are known that are stable at room temperature and atmospheric pressure. However there are reports that high fluoride concentrations increase radon's water solubility (Salih et al. 2004). Radon is far more soluble in organic solvents than in water. This property may lead to a radon accumulation in hydrocarbon contaminants present in the vadose zone or in the aquifer (Hunkeler et al. 1997, Hoehener & Surbeck 2004). Radon decays with a half-live of 3.82 days over several short lived daughter products to the long lived ($T_{1/2}$ = 22 years) nuclide ^{210}Pb (Fig.2). ^{210}Pb from decaying radon present in the water accumulates on flowstone and in cave sediments. It can thus be used for dating.

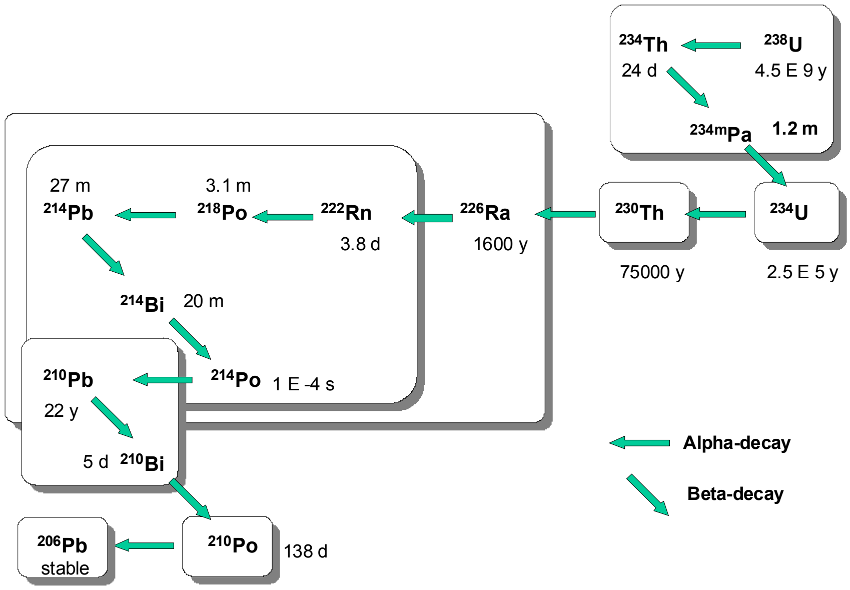

Fig.2 : *238U series*

Gas solubilities are temperature and pressure dependent. Figure 3 shows the solubilities for N_2, O_2, CO_2, Rn and Ar as absolute values at standard pressure (760 mm Hg). Values relative to the concentration at 10°C are plotted in Fig.4. This representation helps to compare the solubility behavior of different gases. It also shows that between 5 and 15 °C a linear approximation with -3.5 % / °C fits the temperature dependence for radon and carbon dioxide well. For O_2, N_2 and Ar a good linear approximation is -2.3 % / °C.

Assuming that there are no chemical reactions with other substances present in the water, gas solubilities are proportional to the pressure in the gas phase. This assumption may not be valid for CO_2 in waters containing dissolved calcium carbonate, especially when they are in contact with solid calcium carbonate.

Total dissolved gas pressure (TDGP) is the sum of the individual dissolved gases' partial pressures plus water vapor pressure. Supersaturation exists when TDGP is larger than the atmospheric pressure. Bubbles can form when TDGP is larger than the atmospheric pressure plus the hydrostatic pressure. Supersaturation may be produced by a temperature increase; as shown above O_2 and N_2 solubilities decrease with temperature at a rate of about 2 % / °C. A temperature difference already exists when infiltration takes place at an altitude considerably higher than the spring (0.6 °C/100 m). Another reason for supersaturation can be that air pockets in the vadose zone are temporally entrapped during high flow and thus be put under hydrostatic pressure. A head of 1 m would lead to a pressure in the air pocket 10 % above atmospheric pressure.

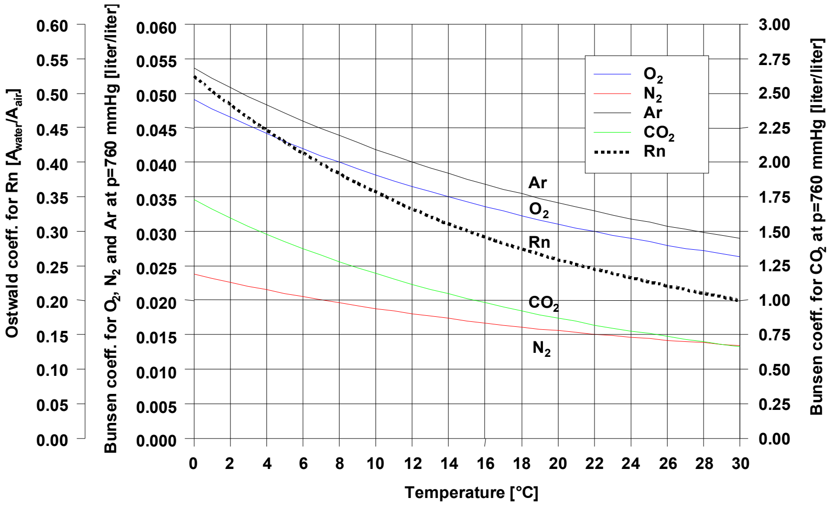

Fig.3 : *Gas solubilities vs. temperature.*

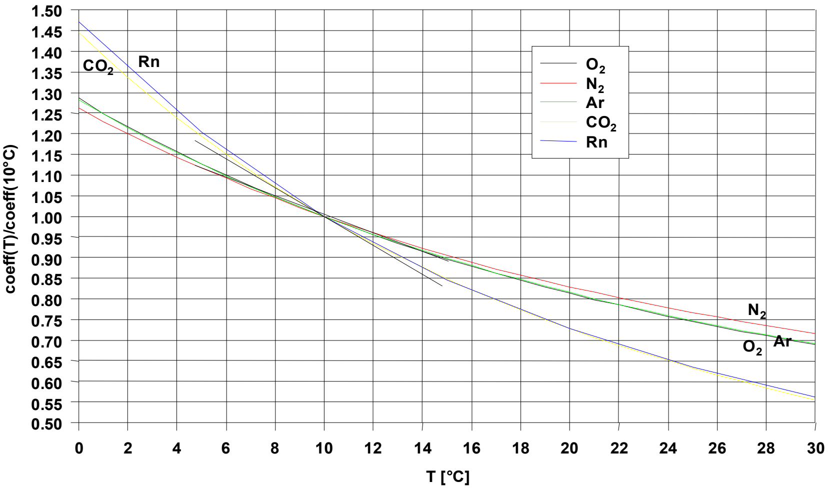

Fig.4 : *Relative gas solubilities vs. temperature.*

How to measure

Radon, batch samples

In the lab but also in the field radon can be measured by bubbling air in a closed circuit through the sample (40 to 250 ml) and then determining the radon concentration in the gas phase (Fig.5).

Radon in water measurement by the “bubbler method”,

batch measurement

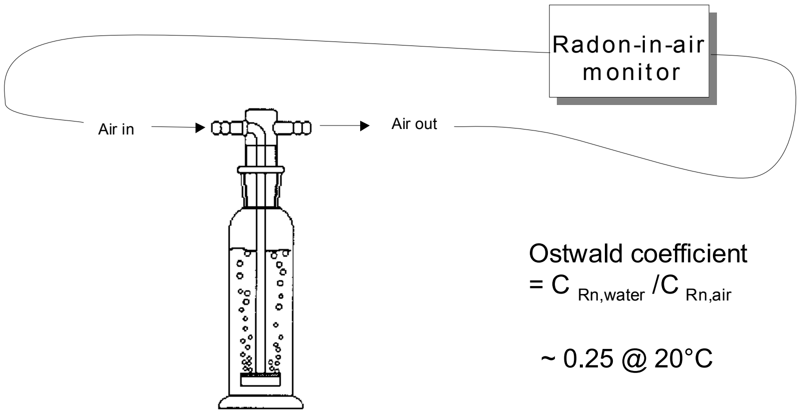

***Fig.5 :** Basic bubbler device for batch samples.*

The air volume should pass at least 4 times through the bubbler to get equilibrium between water and air. This also holds for the CO_2 and methane batch sample measurements described below. Temperature dependence of the solubility has to be taken into account, but with the closed circuit method it' s influence is considerably reduced. There are different detectors for radon in air commercially available. The cheapest ones are passive sensors like track-etch films or electret disks. They have the disadvantage that the result is not immediately available. Among the electronic detectors a system with a Lucas cell coupled to a photomultiplier is still the most sensitive, at a low price. It takes 3 hours until all alpha emitting radon daughter products are built up, but the instrument response function is well known so the measurement can be immediately started after bubbling. However it also takes some time for the radon daughters to decay after purging with fresh air. Both, buildup and decay of the total alpha activity can be approximated by a single exponential with a $T_{1/2}$ of 40 min. There are other electronic monitors based either on a semiconductor detector or an ionization chamber. Those with a semiconductor detector need a large sample volume and an accumulation of the daughter products on the detector by a high voltage to get reasonable sensitivities. They have the advantage that the detector not only counts but has a sufficiently good energy resolution to allow for a discrimination between different radon daughters. Counting only pulses in the ^{218}Po ($T_{1/2}$ = 3.1 min.) energy window avoids the problem of the slow response due to the buildup and decay of the radon daughters farther down in the decay chain.

For most semiconductor radon monitors the gas has to be dried before it enters the instrument. This can be done with an anhydrite (dehydrated calcium sulfate) cartridge. Silica gel should not be used for it not only adsorbs water but also radon. Lucas cells still work well at 100% relative humidity. One only has to avoid condensation inside the cell. Keeping the instrument at a temperature above the sample temperature is all it needs. This can be done by insulating the instrument thermally well. The heat produced inside then keeps the instrument at a temperature slightly above outside temperature.

For all types of instruments used together with a bubbler it is highly recommended to have a Teflon membrane filter at the input to the instrument. This avoids that water can enter the instrument in case of wrong manipulations with the bubbler.

Detection limit depends on the sample quantity and the radon gas detector used. Typically out gassing 40 ml samples allow for a detection limit of about 1 Bq/l, 250 ml for around 0.5 Bq/l.

For large series in the lab the best measurement method is liquid scintillation counting (LSC), if you have access to a an already existing LSC instrument with a sample changer (Tricarb or Quantulus, both now from Perkin-Elmer)). If not, there is an affordable, portable LSC (Triathler, Hidex, Finland), however without a sample changer. For LSC only 10 ml water samples are needed. You can either use a scintillator miscible with water (e.g. AquaLight, biodegradable, Hidex, 10 ml water, 10 ml scintillator) or an extractive scintillator, an organic solvent containing the scintillator (e.g. MaxiLight, biodegradable, Hidex, 10 ml sample + 5 to 10 ml scintillator), that does not mix with water. The advantage of a scintillator miscible with water is that one does not have to wait for the buildup of the radon daughters if the sample has been taken at least 3 hours ago, but detection limit is not better than 1 Bq/l (1 h counting time). Well below that, around 0.2 Bq/l, if really needed, can be achieved by using extractive scintillators and alpha/beta separation and 2 h counting time.

For LSC, 20 ml glass vials with a silicone/Teflon septum are recommended for sampling.

A clever method for sampling radon in wells has been described by Guerin & Vuillemenot (1995). They used silicone stopcocks places at different depths in a well to measure a radon depth profile. Radon is very soluble in silicone rubber.

CO_2, methane, batch sample

Clean outside air contains in the worst case traces of methane and only about 0.04 %vol of CO_2. As for radon, bubbling in a closed circuit and measuring in the gas phase is thus an easy method in the lab and also in the field. A 20 ml sample in a 40 ml vial can be bubbled without a risk for liquid passing too far. Reliable CO_2 and CH_4 sensors use infrared absorption (e.g. Texas Instruments, USA, or RMT Moscow, Russia). A desiccant (anhydrite, not silica gel) is recommended. As for radon the temperature dependence of the solubility has to taken into account. Sampling can be done with the same 20 ml vials as for radon.

Oxygen, nitrogen, TDGP, batch samples

Oxygen and nitrogen are present in the atmosphere so bubbling with air won't work well. There is one sensor that may be used to measure oxygen directly in a batch sample, a fiber optic sensor (Ocean Optics, USA), based on the change of the optical properties of a dye in the presence of oxygen. The fiber can be introduced through a septum into the sample vial, avoiding contact of the sample with outside air. For sampling the same 20 ml vials as for radon can be used. There is no sensor available for nitrogen. When oxygen and CO_2 concentrations and TDGP are know one can calculate the sum of nitrogen and argon, assuming that no other gases are present. Measuring TDGP in batch samples is difficult. Commercially available probes (e.g. Common Sensing, USA) need large sample volumes (>> 1 liter) and avoiding contact with outside air is nearly impossible. We are working on smaller probes.

Oxygen, nitrogen, carbon dioxide and methane all can be measured with a gas chromatograph, even in the field, but it's a quite expensive and delicate instrument.

Continuous measurements

The bubbler used for batch samples can be modified to allow for continuous measurements (Fig.6). Particularilly efficient is to use a water jet pump to equilibrate air and water. Together with a semiconductor type radon monitor temporal resolutions below 15 min can be achieved.

A notorious problem with bubblers for continuous measurements is that pressure differences can build up that push water into the air circuit. A clever solution to this problem has been presented by Burnett. (Burnett et al. 2000).

One can completely avoid this problem by separating the air circuit from the water by a semipermeable membrane (Fig.7). Accurel tubes (trademark of Membrana, Germany) that are used for ultra filtration let pass gases easily, but are watertight up to at about 1 bar. Equilibration between water and air is fast, 50% of the steady state are reached after 9 min. Instead of the very expensive and delicate Accurel

Radon in water measurement by the "bubbler method", continuous measurement

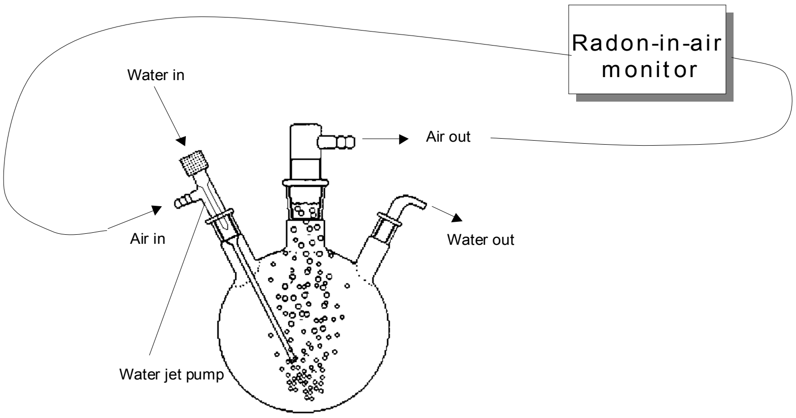

Fig.6 : Modified bubbler for continuous measurements.

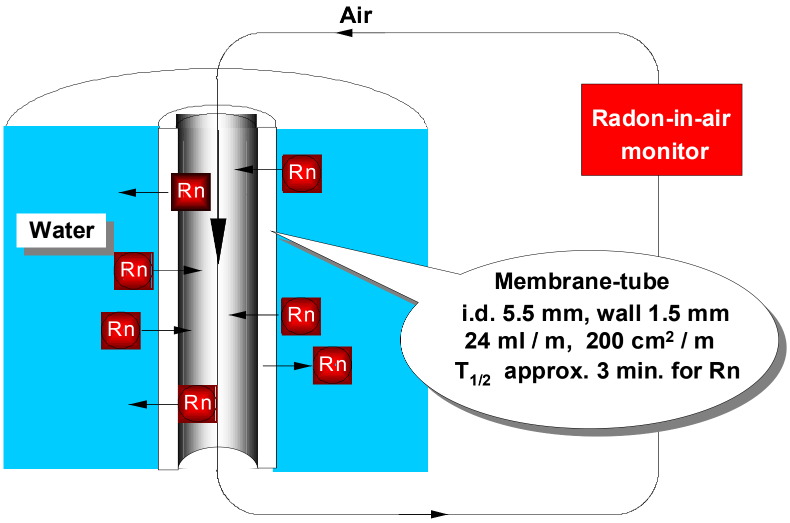

Fig.7 : Use of a membrane tube to couple the air circuit to the water.

one can also use thin walled silicone tubes (e.g. i.d. 4 mm, wall thickness 1mm or smaller). Diffusion through the walls is considerably slower than for Accurel, but still good enough for a temporal resolution of some hours. The slow response is probably not only due to the slow diffusion but also to the fact that radon and CO_2

are very soluble in silicone (Guerin & Vuillemenot 1995). The tube walls thus can store considerable amounts of these gases.

Silicone and Accurel are watertight, but water vapor passes through very well, saturating the air inside quickly. As long as the measuring instruments are at a temperature above the water temperature there will be no condensation. This can be done by insulating the instruments thermally well. The heat produced inside then keeps them at a temperature slightly above outside temperature. This works well in caves where the air temperature is very close to the water temperature. However at springs, mainly at hot springs one has to remove some of the humidity before the air enters the instruments. This can be done with anhydrite cartridges, but they will be used up quickly and at least for Lucas cell detectors there is no need to remove all humidity. One only has to remove some humidity to bring the dew point below the temperature inside the instrument. This can be done with a PermaPure (trademark of Perma Pure LLC, USA) tube immersed in an airtight box filled with silica gel. PermaPure tubes let pass water vapor through their walls but no radon or CO_2. With a 60 cm tube (Disposable Medical Drier, ME060-24MFL) at a gas flow rate of 1 liter/min and at a temperature of 20°C we have measured a reduction of the relative humidity from initially 100 % down to about 30 %. At the gas flow rate and pump cycle we normally use (every 30min, 5 min at 200 ml/min) some 100 ml silica gel will last for months.

As a radon detector we use a Lucas cell based system (Surbeck 1996) coupled to either an Accurel or a silicone tube coil. The air volume inside the coil should be at least as large as the Lucas cell volume. For CO_2 we use the Texas Instruments sensor already described above (full scale either 5 or 25 %). A methane detector based on infrared adsorption can also be placed in the air circuit (e.g. from RMT, Moscow, Russia). Connecting tubes should not be silicone tubes for silicone lets pass radon and CO_2 and also adsorbs these gases.

To measure dissolved oxygen one can either place an oxygen sensor directly into the water or put a sensor in the air circuit. Electrochemical oxygen sensors are notoriously unreliable. Fortunately there are now optical sensors available as described above. They can be placed directly into the water, give very stable values and need no calibration for a whole year (Ocean Optics, USA and Hach-Lange, USA). Another very stable sensor, for the measurement in the air phase, makes use the oxygen's paramagnetic property (Servomex, GB).

Gas solubilities are temperature dependent, thus the water temperature has to be monitored too.

For the measurement of the total dissolved gas pressure (TDGP) about a meter of a thin-walled silicone tube (i.d. 1 mm, wall thickness 0.5 mm), closed at one end and connected at the other end to a pressure sensor is placed into the water (Fig.8). After about 10 minutes a steady state will be reached with the pressure inside the tube being equal to the sum of the partial pressures of the dissolved gases plus water vapor pressure. In our own instruments we measure the difference between the TDGP and the atmospheric pressure with a differential sensor, with one side connected to the tube and the other one to a capillary ending above the water level. An additional sensor outside the water then measures the atmospheric pressure. Other instruments use two absolute pressure sensors, one for TDGP and one for the

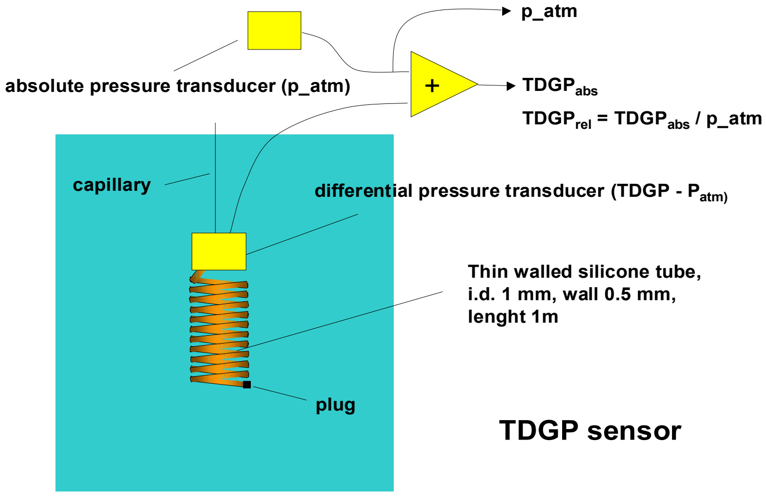

Fig.8 : *Total Dissolved Gas Pressure (TDGP) sensor.*

atmospheric pressure (e.g. Common Sensing, USA). In both cases TDGP is expressed in % of the atmospheric pressure.

Examples for the use of Rn and CO_2 as tracers

As early as in 1918 Perret (1918) reported that the radon concentration in a spring water may depend on the discharge. A generation later, during the hunt for uranium ores, this knowledge seems to have been lost (Payot 1953). Sampling took place as if radon in spring water would be constant over time, depending only on the host rock. Still another generation later, in the wake of alarming news on adverse health effects of indoor radon, radon in water became fashionable again. It started with a serious handicap, the traditional “hard rocker's” view of radon origin, neglecting any soil contribution (e.g. Buchli 1987).

Later, however, Hoehn and Von Gunten (1989) recognized radon´s potential as a tracer to study river water infiltration into a gravel bed. Claims about the importance of soil radon for the radon concentration in karst waters were published in 1992 (Surbeck & Medici 1991), but Monnin et al. (1994) still considered deposits in karst channels and in fractures a possible radon source.

Monthly sampling of 15 springs in western Switzerland, most of them karst springs, during 1993 and 1994, showed large temporal variations (Fig.9) and in general a positive correlation between radon concentration and discharge. First continuous measurements (Surbeck 1993, Surbeck & Eisenlohr 1993) confirmed the claim that the radon produced in the soil covering a karst system is the most important source for radon peaks observed during storms (Eisenlohr & Surbeck

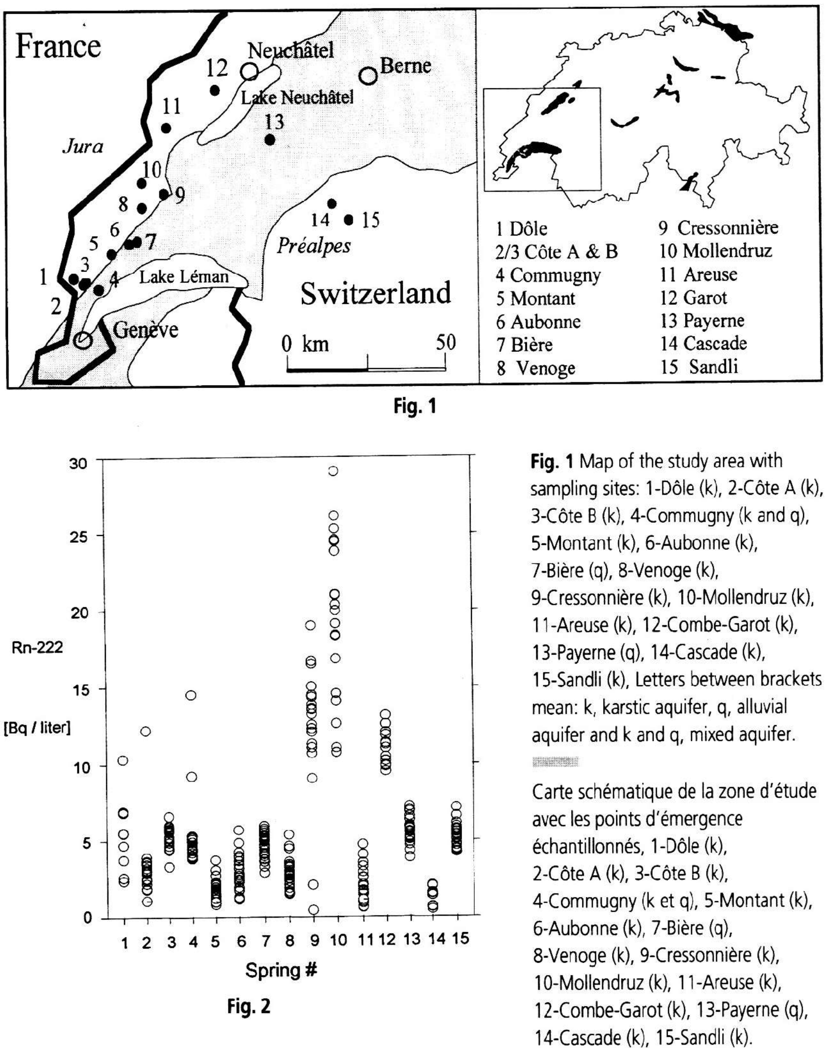

Fig. 1 Map of the study area with sampling sites: 1-Dôle (k), 2-Côte A (k), 3-Côte B (k), 4-Commugny (k and q), 5-Montant (k), 6-Aubonne (k), 7-Bière (q), 8-Venoge (k), 9-Cressonnière (k), 10-Mollendruz (k), 11-Areuse (k), 12-Combe-Garot (k), 13-Payerne (q), 14-Cascade (k), 15-Sandli (k), Letters between brackets mean: k, karstic aquifer, q, alluvial aquifer and k and q, mixed aquifer.

Carte schématique de la zone d'étude avec les points d'émergence échantillonnés, 1-Dôle (k), 2-Côte A (k), 3-Côte B (k), 4-Commugny (k et q), 5-Montant (k), 6-Aubonne (k), 7-Bière (q), 8-Venoge (k), 9-Cressonnière (k), 10-Mollendruz (k), 11-Areuse (k), 12-Combe-Garot (k), 13-Payerne (q), 14-Cascade (k), 15-Sandli (k).

Fig.9 : *^{222}Rn in monthly samples from springs in Western Switzerland. From Eisenlohr & Surbeck 1995.*

1995, Fig.10). Increase of the radon concentration turned out to be a clear indicator for the arrival of water from the soil.

A new generation of our radon monitor, with the bubbler replaced by a membrane tube and all trimmed to low power consumption and to resist adverse conditions made it possible to start continuous measurements even in caves. A CO_2 sensor has been added. We thus make use of two different natural tracers, both produced in the soil, but with different physical and chemical behavior.

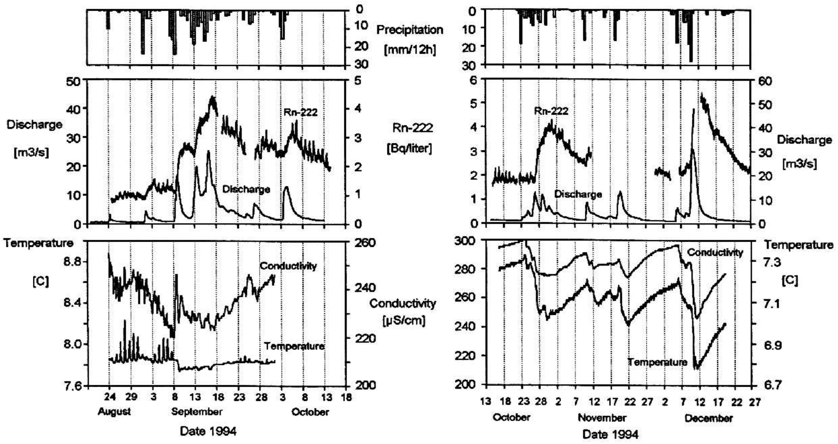

***Fig.10** : Continuous measurements at the Areuse spring. From Eisenlohr & Surbeck 1995.*

At two sites continuous radon and CO_2 measurements have been done for about 2 years. The first site (Milandre) is at an underground karst river in the Jura Mountains. It has a well defined, small (around 10 km^2) catchment area at an altitude of about 400 m above sea level. The soil is several meters thick and well developed, with few residual carbonate remaining. There is clear evidence for an important epikarst layer. The second site is at a karst spring in the Swiss Alps (Neirivue). The catchment area is far larger than at Milandre, on the order of 100 km^2, and infiltration altitudes range from about 800 to over 1500 m above sea level. Soil is not well developed or even missing.

At both sites radon concentrations increase after a storm, with the radon concentration decreasing slower than the flow, pointing to a recharge of the karst system with radon rich water. Examples for the Neirivue site and the Milandre site are shown in Fig.11. Absolute radon concentrations for the two sites are clearly different, a result of the differences in soil cover. For the same reason CO_2 concentrations are different. Common to the two sites is, that CO_2 concentrations are lower during the winter than during the summer, due to the temperature dependent biological activity.

Figure 12 shows Rn and CO_2 reaction to two successive storm events after a long dry period. The first event, a minor one, puts pressure on the system, pushing water stored in the epikarst down to the saturated zone. Water stored in the epikarst from previous storm events has lost it's radon by radioactive decay, but CO_2 is still present. Thus at the underground river CO_2 concentration increases without an increase in the radon concentration; water from the epikarst has arrived. The second, more important storm inputs enough water to flush the soil, leading to an increase in the radon concentration; a clear sign of water that has recently been in contact with the soil. Both radon and CO_2 concentrations decrease after the storm, radon

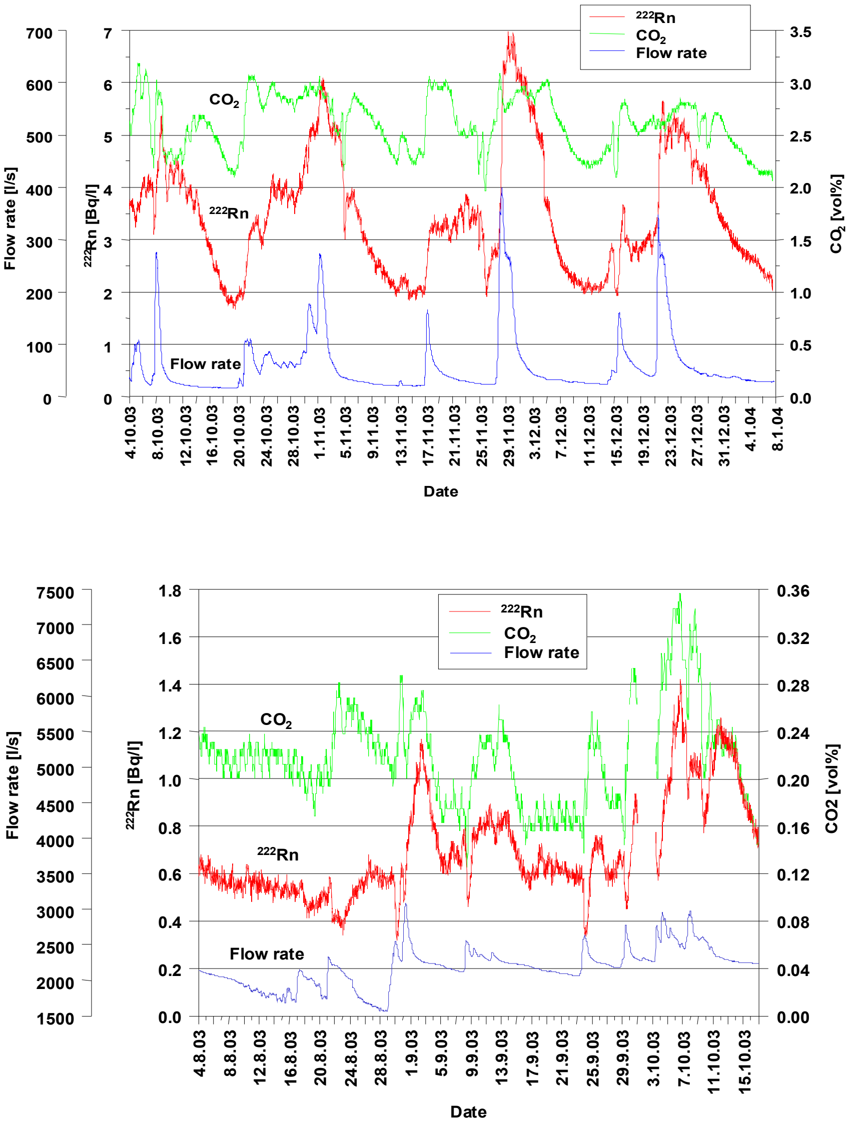

Fig.11: *Continuous radon and CO_2 measurements at the Milandre underground river (above) and the Neirivue spring (below).Measurement uncertainities for Rn and CO_2: ~5%*

decays with a half-live close to 4 days and CO_2 reacts with the limestone. CO_2 "half-live" in the Milandre system seems to be around 11 days.

We thus can discriminate between different origins of the water at the underground river, using electric conductivity as an additional parameter :

a) low radon, low CO_2, high conductivity --> water having been for a long time in contact with the limestone, more than a month.
b) low radon, high CO_2, medium to high conductivity --> water from the epikarst.
c) high radon, high CO_2, medium to high conductivity --> water from the soil.
d) low radon, low CO_2, low conductivity --> rainwater, that has found a fast way down, e.g. through sinkholes.

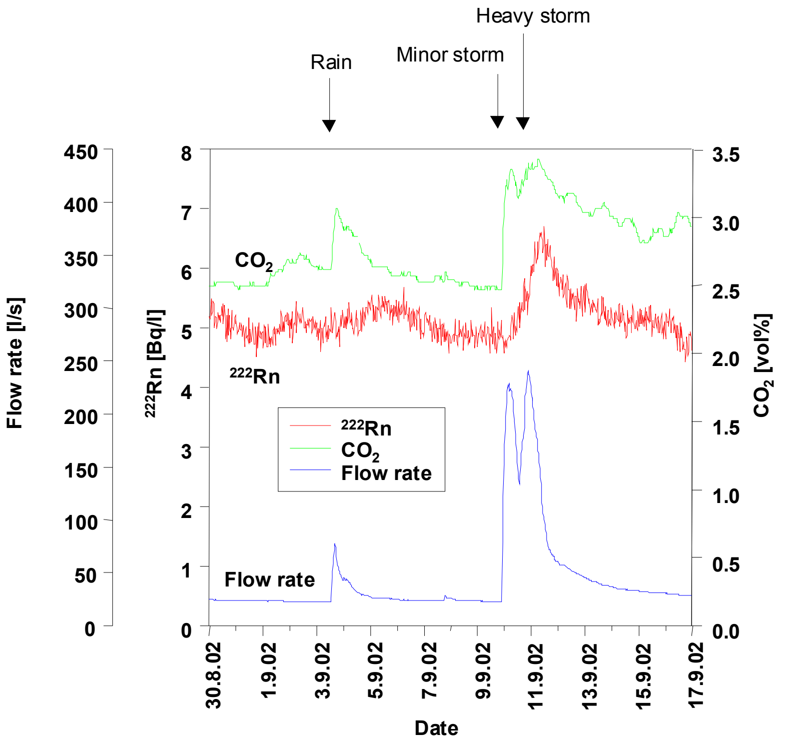

Fig.12 : *Reaction to storm events at the Milandre site.Measurement uncertainities for Rn and CO_2: ~5%*

At the Milandre site we have measured for some months not only radon and CO_2 in the water but also in the cave air. Both radon and CO_2 in the cave air follow with a delay of some hours changes in the concentrations in the water. Concentrations in the cave air are at maximum at what would be expected for equilibrium between water and air, but in general below these values. These data clearly show that water is the source for radon and CO_2 in the cave air, as claimed before (Surbeck & Medici 1991); it's not the other way round.

An example for supersaturation

The Neirivue spring feeds a fish farm (trouts). In the early days of this farm there have been serious problems during high flow periods with supersaturation leading to “bubble disease”. The problem has been eliminated with the help of a device mixing water intimately with outside air, thus considerably reducing supersaturation.

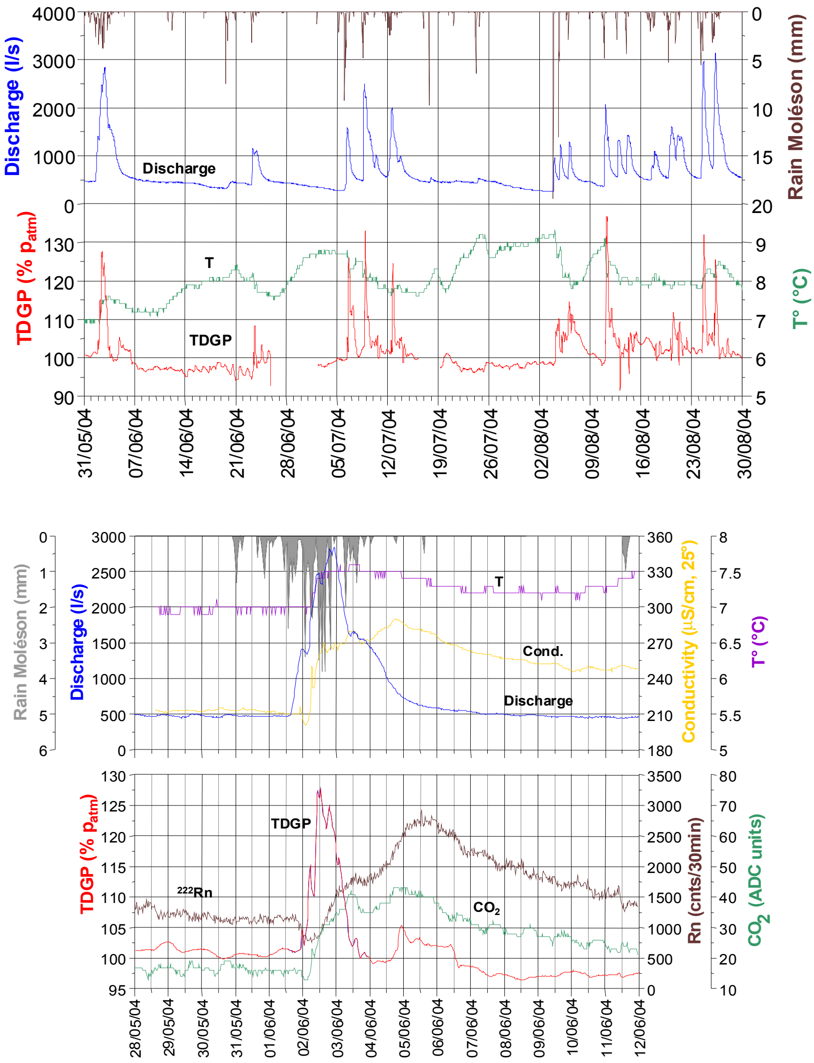

Fig.13: *Continuous radon, CO_2 and TDGP measurements at the Neirivue spring. 30 min interval. Measurement uncertainities : Rn, CO_2: ~5%, TDGP : ~1%.*

Former batch measurements done by the farm owner, using a simple mechanical pressure gauge already have shown that supersaturation rises near peak flow and only lasts some hours. Our continuous measurements (30 min. interval) have confirmed this and show that the peaks are very sharp and that there is no correlation between TDGP and radon or CO_2 (Fig.13). We assume that these supersaturation peaks are due to a clogging of parts of the conduits (vadose zone) during high flow. Entrapped air then gets compressed by the water column above, leading to more gas dissolved.

Batch TDGP measurements at other Swiss karst springs showed that supersaturation may be rather the rule than the exception.

Continuous TDGP measurements at the Milandre site however showed nearly no reaction to even extreme storm events. The thick soil cover there probably damps reaction to storms so conduits won't be clogged. The Milandre data are somewhat in contrast to observations made by Holocher et al. (2002) on laboratory soil columns. They report considerable supersaturations ("excess air") during recharge, due to the dissolution of entrapped air bubbles under hydrostatic pressure.

Supersaturation clearly deserves more attention from the hydrogeology community. Simple things like measuring electrical conductivity become unreliable in supersaturated waters. Bubble formation on measuring electrodes may produce completely wrong readings.

How high radon concentrations may be produced

This short note is about how high radon concentrations may be produced. It is less about karst for until now we did not measure really high radon concentrations (> 50 Bq/l) in Swiss karst springs. This may be different in other countries, e.g. in Hungary there are karst springs known with up to some 100 Bq/l. Although there is still a firm believe around there about a deep origin of this radon, I'd like to present an alternative model.

As mentioned in the context of soil gas radon, radium adsorbed on iron hydroxides makes an excellent radon source. This has already been noticed by radon pioneers like Mache (Mache & Bamberger 1914, Job & Zötel 1969) when trying to explain high radon concentrations in the Bad Gastein springs in Austria.

Combined radon and ^{226}Ra measurements on thermal waters in Aix-en-Provence (Lettry 2002) showed a negative correlation between the two nuclides and a positive correlation between ^{226}Ra and the temperature. Upwelling anoxic thermal water mixes with cold, oxygen rich water. This leads to iron hydroxide precipitation scavenging ^{226}Ra from the thermal water and thus forming an efficient radon source (Fig.14). Several studies in Switzerland on high radon concentrations (up to 650 Bq/l) in springs emerging from various geological formations, crystalline as well as sedimentary, all support this conceptual model (Gainon 2003, Schott &

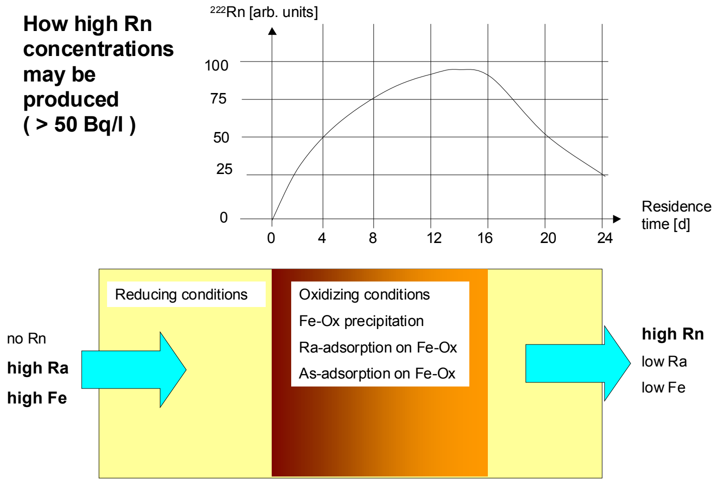

Fig.14 : Conceptual model for high radon production.

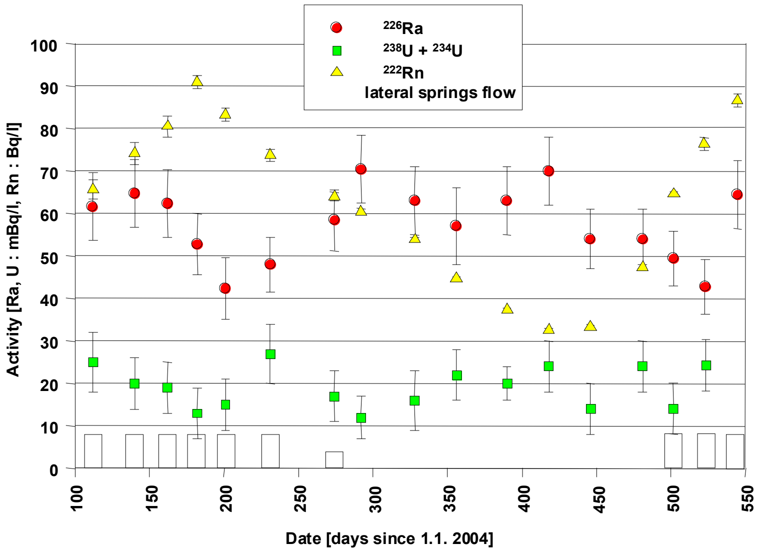

Fig.15 : Time series for the "Source de Leytron" thermal spring.

Wiegand 2003, Deflorin 2004, Kloos 2004). Large seasonal variations in the radon concentration of a thermal spring in the Valais, Switzerland, can also been explained that way (Fig.15). These variations can't be due to changes in the mixing ratio of the thermal and the cold component, for the temperature varies only between 23.6 °C and 24.2 °C over the whole year. Radon concentrations rise with the onset of snow melting that increases hydrostatic pressure. This probably forces the water to pass through a more important volume with iron hydroxide precipitations and thus leads to an increase in the radon concentration.

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I would like to thank Frédéric Bossy, François Bourret, Laurent Eisenlohr, François Gainon and Ludovic Savoy for their help in the field and for clarifying discussions. A large part of the work presented has profited from a contract with the Swiss Federal Office of Public Health.

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