Using ^{222}Rn for hydrograph separation in a micro basin (Luxembourg)

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Abstract
In order to obtain information on the hydrological signature of rivers during and after heavy rain events, small catchment areas are selected as experimental sites. Hydrograph separations based on environmental tracers are performed. Natural isotopic tracers such as ^{18}O, ^{2}H and particularly ^{222}Rn may help to distinguish the components dominating the outflow, particularly of 'pre-event waters', 'event waters' and 'post-event waters'. Even with moderate concentrations in groundwater, radon can be a very sensitive indicator of groundwater input into rivers. The selected microbasin under investigation is situated in the western part of Luxembourg and belongs to the Attert River catchment. At chosen points at the basin's outflow radon detectors continuously measure radon activity in water. The radon monitors are installed together with high precision thermometers, conductivity meters, flow meters and automatic water samplers for chemical analysis. Besides the continuous measurements, grab water samples are taken at different locations along the stream, most of them during periods of heavy rain events. Presented are the results of a one year measurement campaign. During the dry season *i.e.* during more or less continuous discharge conditions, the observed mean values do not show substantial variations and can be used as reference values. Fluctuations of the measured data during rain events are discussed and the interplay between the different parameters analysed.

Key words *radon – hydrology – tracer – hydrograph separation*

1. Introduction

Naturally occurring isotopic and chemical tracers are among the most useful tools in the study of river flow generation. Such tracers are often applied in the context of simple mixing models that attempt to separate the relative contributions to river flow from different geological reservoirs. A well-known example is the use of ^{18}O or ^{2}H to separate storm river flow into 'new' water (storm precipitation) and 'old' water (pre-storm subsurface water) (*e.g.*, Sklash *et al.*, 1976; Hooper and Shoemaker, 1986).

The understanding of hydrological flow and river flow generation has gained an increasing importance in a wide range of studies for water resource, contaminant transport and geochemical and even biochemical issues. In the last 40 years, many publications have tried to elucidate the mechanisms by which water is collected in catchments and how it moves down hillslopes into small rivers (Hoehn *et al.*, 1989). Among the many methodologies, those involving naturally occurring tracers have become important.

Tracer studies generally lead to the separation of river flow into two or more components and eventually, through the radioactive tracers like anthropogenic tritium, natural radon and radium isotopes, give an estimation of the groundwater residence times. Numerous studies demon-

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strate the utility of the stable hydrogen isotope deuterium ^{2}H and the stable oxygen isotope ^{18}O. Studies involve other tracers like calcium (Genereux *et al.*, 1993), silicium and various other major ions, depending on the ionic strength of the waters and their possibility to acquire substantial amounts of those elements from the soil and rocks.

Many of common tracer studies focus on the effect of storm flow, the most common type of analyses being a separation of hydrographs into 'old' water present in the watershed before the start of the rain event and the 'new' water mixing in during the event of interest.

For the study of river flow generation it is unrealistic to expect that whatever tracer methods are applied, all the answers to the important questions concerning hydrological flow paths on watersheds and information on the water movement in a catchment during a rainfall-runoff event are given. It is in applying multiple field techniques that an optimal approach can be achieved.

In the CYCLEAU project the aim is to use a multifunctional approach. In the present paper only the involvement of the tracer element radon together with temperature and electrical conductivity are presented and discussed.

Differences in radon content of subsurface waters arise from differences in radon emanation by porous media (bedrock or soil) and from the differences in the degree of subsurface degassing. The factors influencing the behavior of ^{222}Rn in the subsurface have been the subject of numerous investigations (*e.g.*, Clements and Wilkening, 1974; Schery *et al.*, 1984 for the elder references) and are not part of the present paper. Here we expect only markedly different radon concentrations in the natural waters, especially corresponding to zones of unsaturated and saturated soils.

Simple three-end-member mixing models may provide a useful framework for riverflow generation, the three different waters being superficial water (vadose zone water), soil ground water and bedrock water (Genereux *et al.*, 1993). Merot *et al.* (1995) suppose a four-component hydrograph separation in studying the complex variations of groundwater, riparian zone seepage, hillslope subsurface flow and event water.

^{222}Rn can be useful in distinguishing between saturated zone water and unsaturated superficial water; the former usually has a much higher radon content than the latter. Water in unsaturated zones may lose much of its radon to the atmosphere by degassing to soil air, whereas water in saturated zones generally retains most of its radon. Superficial water that enters a saturated zone begins to accumulate ^{222}Rn, acquires the ^{222}Rn signature of the rock and soil underground at a rate controlled by the retention time and the radioactive decay.

Superficial water having been in a saturated zone for several days can be considered groundwater. Radon can reach relatively high concentrations in groundwater but, because of its low solubility, it degasses rapidly in surface waters. Therefore it can be a very sensitive indicator of groundwater input to streams.

The ^{222}Rn content of river water is strongly affected by volatilization to the atmosphere, and this must be accounted for in using radon data to estimate a possible groundwater influx from subsurface water sources, important in river flow generation. In the following we consider a given length Δx of a river and two sampling sites at the upstream and downstream ends. A simple one-dimensional model equation can be proposed as

$$Q_2[\mathrm{Rn}]_2 = Q_1[\mathrm{Rn}]_1 + q\Delta x\,[\mathrm{Rn}]_q - \tau k Q_{\mathrm{avg}}[\mathrm{Rn}]_{\mathrm{avg}}$$

where Q (m^3/s) is the river discharge, the subscripts 1 and 2 designate the upstream and downstream ends, q ($m^3s^{-1}m^{-1}$) the inflow rate per unit of river length, τ the travel time, k a radon-degassing rate constant; Q_{avg} and $[\mathrm{Rn}]_{\mathrm{avg}}$ are the mean river discharge and the mean radon volumetric concentration in the stream. We assume that the length is sufficiently small allowing the same radon concentration for lateral inflowing water.

As the travel time is very short, a loss of radon due to decay (T = 3.8 d) is negligible. Due to the turbulent runoff of the small rivers, the primary mechanism of radon removal is gas exchange.

2. Material and methods

To obtain information on the hydrological signature of small rivers during and after heavy

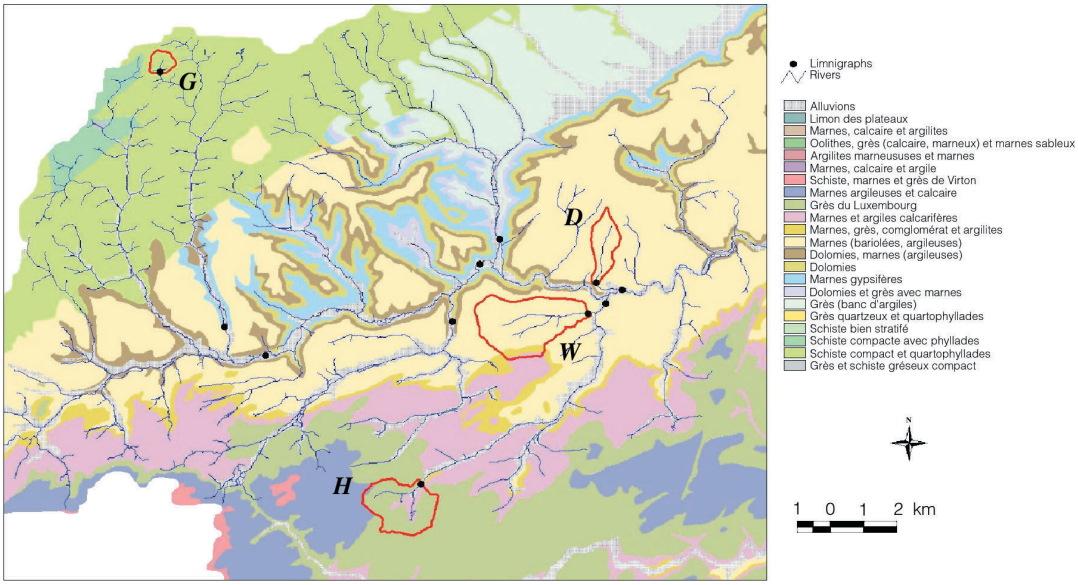

Fig. 1. Map of the catchment areas of the Attert River, shown are the four micro basins under study. The present work concerns micro basin *H*.

rain events, four small catchment areas of the same river were selected as experimental sites. Ephemeral or first-order streams drain those watersheds of 10-100 ha. The selected sub-catchments under investigation are situated in the western part of Luxembourg and belong to the Attert River Basin, the latter being integrated in the European Network of Experimental Research Basins (ERB).

The catchment area of the river basin is 318 km^2. The altitudes vary from 540 m to 210 m, with slopes presenting a maximum of 16°. The geological underground is formed of Devonian schist in the highest northern part, Triassic marls und mudstones for the middle part and Liassic sandstones for the southern part.

The present paper concerns the micro basin *H* (fig. 1), located in the southern part of the Attert Basin. It is covered to 93% by forest and 7% by pasture; the underlying rocks and soils are over 81% sandstone, 13% marls, 3% marls/mudstones and 3% alluvium deposits. The topography stratifies the watershed into two subunits, hilltops and valleys, with altitudes between 380 and 320 m.

2.1. *Radon in water measurements*

Liquid Scintillation Counting (LSC) is used for the determination of α-emitters in environmental samples. Presently, this technique is used for radon and radium in water measurements. For radon measurements, normally 14 ml of water are mixed to 7 ml of scintillation cocktail Betaplate, out of which 5 ml are counted in the Triathler portable liquid scintillation device. This device provides efficient alpha-beta discrimination. For the very low concentrations of river water, the sample volume is increased to 250 ml, thus a limit of detection down to 50 mBq/l can be obtained. Samples are prepared by carefully introducing the water under the cocktail prepared in a glass vial. Measurements are performed after a waiting time of at least 3 h, permitting equilibrium between radon and the decay products.

Concerning continuous radon-in-water measurements, for radioprotection purposes, a detection limit of 10 Bq/l is needed, but for hydrogeological studies detection limits lower than 1 Bq/l are required. When deciding which

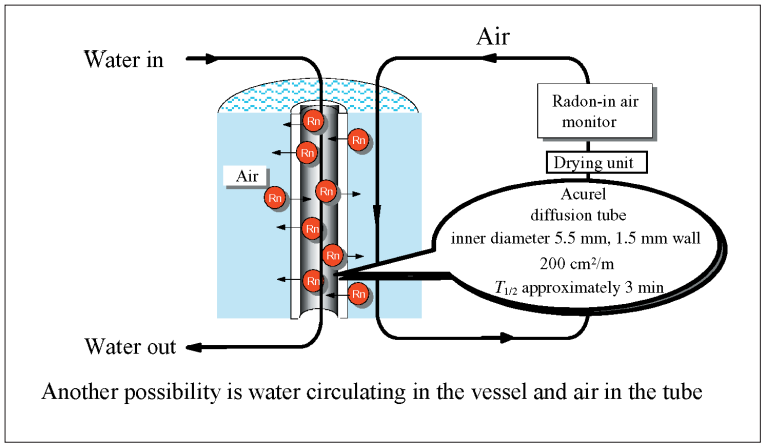

Fig. 2. Principle of the use of an Accurel diffusion tube for radon-in-water measurements (Surbeck, 1996).

method to use, an important point is how much measuring time is necessary to obtain an acceptable precision and give a signal that significantly differs from the background.

Radon concentrations in a spring can vary considerably with time. The sampling frequency has to be adapted to the dynamics of the corresponding aquifer. However, one rarely knows how fast an aquifer will react to changing environmental conditions, *e.g.*, to heavy precipitations. Extreme cases are karst springs where discharges are reported to increase by two orders of magnitude within hours after a storm (Eisenlohr and Surbeck, 1995). Even springs emerging from an aquifer containing old water may react quickly to precipitation because of a rapid change in hydraulic pressures. In order not to miss important features, our continuous radon-in-water monitors have a temporal resolution of half an hour. There are several possibilities to monitor radon continuously in water. We decided to use the principle of radon gas measurements in a closed circuit coupled to the water. The coupling consists either in bubbling air through the water, or replacing the bubbling facility with a diffusion tube (fig. 2). In combining the degassing unit or the diffusion tube with a radon detector based on ^{222}Rn and ^{218}Po, it is possible to have a resolution below 1 Bqm^{-3}. This is necessary if one wants to monitor continuously radon concentrations in river water far away from the sources where nearly all of the radon has degassed. If one puts the diffusion tube into the water it is essential to have a high water flow as a depleted or enriched zone exists around the diffusion tube, not having the same radon concentrations as the water flowing in. In order to avoid this drawback we let water circulate in the tubing, measuring the radon concentration in the vessel, either by putting a small radon monitor (DoseMan, Sarad company, Dresden) into the exchange vessel, or pumping the air from the exchange vessel to the measuring chamber of the radon monitor. As the semiconductor devices normally have to work under dry conditions, air passes a drierite column prior to counting. Another drawback with the diffusion tube is the change in the Oswald coefficient with temperature. Water temperature has to be measured and a correction performed. Preferably we use the diffusion-tube method to monitor the water at springs where temperature variations are small.

Temperature and conductivity measurements are performed each time a grab sample is taken for radon measurements. Continuous radon measurements are always coupled with continuously working thermometers and conductivity meters. A locally installed weather station informs on atmospheric parameters, namely rainfall.

3. Results and discussions

To quantify the influx of groundwater to surface discharge, it is necessary to define a typical ^{222}Rn value for the groundwaters of the basin. This value was established by measuring the ^{222}Rn concentration of a number of springs in the investigated microbasin (table I). Radon concentrations in the springs entering the river range between 10 and 25 Bq/l, which is about a factor 10 higher than river radon concentrations.

Spring water is generally collected less than 1 m from the point where it first emerged from the ground. Degassing over a short distance can be admitted as insignificant, and no volatilization correction has to be applied to ^{222}Rn spring water. Nevertheless, if the water output is on a hillside, often prior to the physical output, radon degassing may occur due to underground turbulent flow and small water cascades.

Table I. Summary of results of radon measurements in 8 sources of the catchment area under study.

Location	No. of meas	mean (Bq/l)	min (Bq/l)	max (Bq/l)
*H*4	14	13	9.6	15
*H*5	9	23	22	25
*H*6	14	4.8	2.8	8.4
*H*8	14	10	6.8	12
*H*10	12	16	9.5	19
*H*11	14	12	11.0	14
*H*17	7	13	10.6	14
*H*18	6	14	12.0	17

Figure 3 shows the temporal evolution of radon concentrations measured at 8 sources. During this period no major rain event was observed and the radon concentrations do not experience wide variations. Nevertheless a rainy period at the end of August and at the end of November induced a slight increase in radon concentrations.

Figure 4 shows radon concentrations measured during a December rainy period at the outlet of the microbasin. Among the data, most interesting are those documenting continuous measurements of radon, electric conductivity and temperature; barometric pressure did not influence the measured data. The data of fig. 4 were collected at the outflow point *H*1 of the microbasin under study. For the period under investigation, every major rain event induced a rapid decrease of the electric conductivity and an increase in radon concentrations.

Often a time lag between conductivity and radon is observed. The drop in conductivity is due to the input of superficial water to river water, whereas increased radon concentrations are due to groundwater. Infiltrating water to the aquifer has a piston effect on residential groundwater in the fracture systems close to the main underground pathways and canals. Radon-rich water is pressed out of the fracture system and enters the river, sometimes with a time delay to the conductivity, the lat-

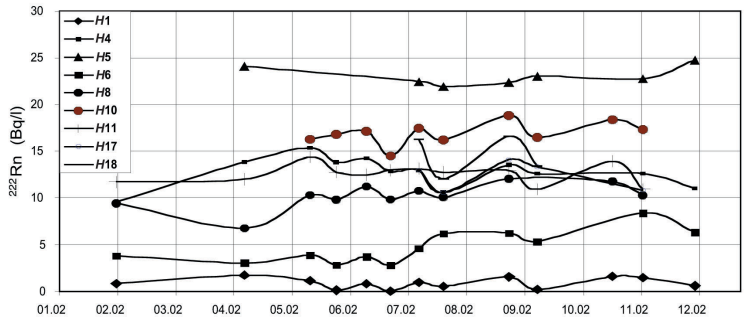

Fig. 3. Variations with time of the grab-samples taken at different sources (with concentrations higher than 10 Bq/l) and at 2 points along the river (*H*1 and *H*6).

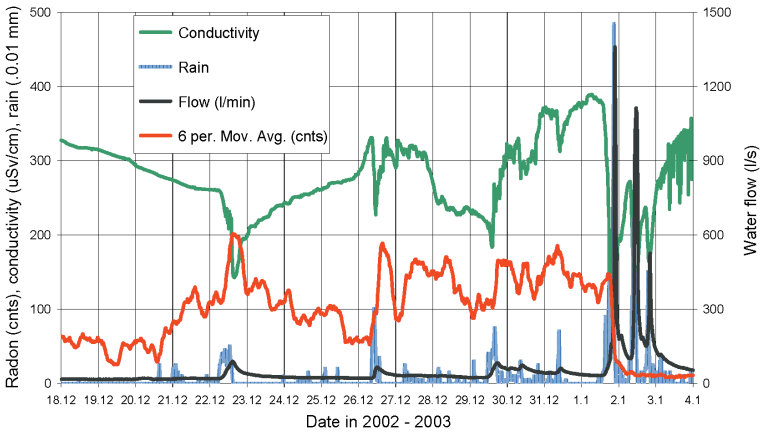

Fig. 4. River water radon and conductivity *versus* time measured at *H*1, the outflow of the microbasin area. Very high water levels, consecutive to a very strong rain event on 2nd January 2003, upset the radon measuring device. Radon concentrations measured after are those of outside air.

ter tracing the direct superficial flow. Radon peaks, consecutive to a rain event, last much longer as do conductivity lows thereby documenting a difference in their contribution of hillslope subsurface and groundwater or superficial runoff water.

There exists an apparent contradiction between the hydrometric evidence of rapid flow along surface and near-surface pathways and the radon evidence of a high portion of old water contributing to storm flow. Storm flow generation results in a rapid increase in groundwater level increasing the hydrostatic pressure and thus the underground flow in near channel areas (Mulholland, 1990). One can expect higher radon concentrations at the output as water normally retained in underground fracture zones close to the main flow channels is pushed into the flow channels.

4. Conclusions

Radon occurs naturally in all groundwater with varying concentrations depending on lithology and geological structure. Here we describe a methodology that uses ^{222}Rn to provide information on river inflows by admitting that water from different pools contributing to riverflow differs in ^{222}Rn concentration. Superficial water has a markedly different radon content from groundwater, the latter differing in radon concentrations if originating from saturated soils or from fractures in the bedrock. Levels of ^{222}Rn found in rivers are at least one order of magnitude lower than the associated groundwater concentrations, thus radon is a sensitive way of detecting groundwater inflow. ^{222}Rn data can be used in a simple mass-balance equation in conjunction with river discharge data to quantify groundwater inputs to surface flow. In addition, in order to allow the location and quantification of groundwater and surface water deliveries, independent estimates of groundwater discharge and recharge or aquifer storage capabilities are possible.

The response of a forested watershed to advective rain events is the main purpose of the present study. The results, even if preliminary, are very promising and partly illustrate the given objectives.

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