Determination of radionuclide levels in rainwater using ion exchange resin and γ-spectrometry

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The evaluation of radioactivity accidentally released into the atmosphere involves determining the radioactivity levels of rainwater samples. Rainwater scavenges atmospheric airborne radioactivity in such a way that surface contamination can be deduced from rainfall rate and rainwater radioactivity content. For this purpose, rainwater is usually collected in large surface collectors and then measured by γ-spectrometry after such treatments as evaporation or iron hydroxide precipitation. We found that collectors can be adapted to accept large surface (diameter 47 mm) cartridges containing a strongly acidic resin (Dowex AG 88) which is able to quantitatively extract radioactivity from rainwater, even during heavy rainfall. The resin can then be measured by γ-spectrometry. The detection limit is 0.1 Bq per sample of resin (80 g) for ^{137}Cs. Natural ^{7}Be and ^{210}Pb can also be measured and the activity ratio of both radionuclides is comparable with those obtained through iron hydroxide precipitation and air filter measurements. Occasionally ^{22}Na has also been measured above the detection limit. A comparison between the evaporation method and the resin method demonstrated that 2/3 of ^{7}Be can be lost during the evaporation process. The resin method is simple and highly efficient at extracting radioactivity. Because of these great advantages, we anticipate it could replace former rainwater determination methods. Moreover, it does not necessitate the transportation of large rainwater volumes to the laboratory.

1. Introduction

Radionuclides released into the atmosphere can be deposited on soil and vegetation through different mechanisms, including wet deposition. It is now well known that a relationship exists between the ^{137}Cs deposition (Bq m^{-2}) following the Chernobyl accident and the rainfall rates during the week of the event in Western Europe (Clark and Smith, 1988; MacAulay and Moran, 1991; Renaud et al., 2003; Talerko, 2005). Schuller et al. (2002) have demonstrated a linear relationship between ^{137}Cs deposition on soil from global fallout and the annual precipitation rate. In addition Pourcelot et al. (2007) have demonstrated a relationship between the ^{90}Sr from nuclear bomb testing detected in milk and the altitude of grazing. The relationship between rainfall (inc. snowfall) and altitude being well established (Touazi et al., 2004), the above examples evince the necessity of radionuclide determination in rainwater for evaluating potential radioactivity contamination of the environment and for correctly evaluating the extent of soil contamination. Moreover, interception and initial retention of wet deposition by vegetation are an essential mechanism in food contamination that necessitates the determination of rainfall rate and rainwater radioactivity content for dose assessment of the population after an accidental release of radioactivity into the atmosphere (Hoffman et al., 1995).

In spite of this requirement few developments have been made to facilitate rainwater radioactivity determination. Most of the existing techniques rely on the use of large rainwater collectors (usually a collecting surface of 1 m^2) followed by γ-spectrometry, either directly or after the evaporation of larger samples (typically 5 l) or after iron hydroxide precipitation (Caillet et al., 2001; Ioannidou and Papastefanou, 2006). Komura et al. (2007) used a combination of strongly acidic cationic and anionic resins in batch extraction of ^{24}Na, ^{28}Mg, ^{38}S, ^{38}Cl and ^{39}Cl from larges volumes (50 l) of rainwater before performing ultra-low-background γ-spectrometry. Nevertheless, little data exists regarding the risk of activity loss during evaporation, through absorption on vial walls, or of any bias in γ-spectrometry measurements due to the settling of airborne particles whose

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typical size is 1 μm in diameter (Measday and Ho, 2004) during the measurement. In fact, airborne radioactivity concentration and monthly regimes of precipitation have been demonstrated to be anti-correlated (Alonso-Hernàndez et al., 2004) which implies that most rainwater activity is particle-associated. In this respect rainfall radioactivity has been found to be diluted by long rainfall event in comparison to shorter rainfall event. Thus activity has been found mainly in the first aliquots sampled during longer rainfall event (Ioannidou and Papastefanou, 2006). Indeed, Papastefanou et al. (2001) found that colored rain dust from the Sahara Desert collected on roofs in the Thessaloniki area (Northern Greece) not only contained ^{137}Cs from Chernobyl and terrestrial ^{40}K but also high levels of cosmic-ray produced ^{7}Be (>4 kBq/kg). This shows that atmospheric ^{7}Be can be efficiently scavenged by rain dust. In contrast, Livens et al. (1992) have demonstrated that dry deposition is much more effective in scavenging ^{131}I, possibly due to charge repulsion of this anionic species from negatively charged aerosol particles.

In our laboratory (Radioprotection, Consumer Protection, Federal Office of Public Health, 3003 Bern), the rainwater radioactivity measurements are traditionally carried out by γ-spectrometry after evaporation of the samples. This work involves transporting large water samples (usually 5 l) from different places in Switzerland to the laboratory followed by a lengthy evaporation process. Moreover, as the evaporation is conducted without tracers or carriers, any loss incurred during the evaporation process is not taken into account. Thus, in this project, we propose a simple modification to our classic rainwater collectors in order to direct the water flow into a large diameter cartridge (47 mm) containing a strong acidic cation exchange resin (Dowex AG 88). This resin is characterized by a high capacity (1.7 meq g^{-1}), a fast exchange rate, a satisfactory difference in relative selectivity against H^{+} for most of the cations (Table 1) and a low cost. After exposure to rainfall events, the cartridge is sent to our laboratory where the resin is homogenized, then transferred into a geometry calibrated for γ-spectrometry.

2. Material and methods

Resin (Dowex AG 88) was obtained from Aldrich Chemical Company Inc. U.S.A. Water containing radioactive elements (^{54}Mn, ^{58}Co, ^{60}Co, ^{137}Cs, ^{65}Zn), used to simulate contaminated rainwater, was obtained from the cooling systems of various Swiss nuclear reactors. Water samples were kept acidic (pH < 5) as average worldwide pH value of rainwater is below 5.0, thus avoiding hydrolysis of metal cation species (Krämer et al., 1996; Grömping et al., 1997). Rainwater collectors and resin cartridges were homemade devices whose characteristics are presented in Fig. 1.

Extraction experiments (stable potassium and cesium) were carried out by connecting a 10 l vial containing 200 mg of K and 200 mg of Cs to the cartridge. Elution rate was about 0.65 l per minute. Elution of K and Cs from the resin was made in 5 M HCl. K and Cs content in the solution before and after its passage through the cartridge was determined by atomic emission spectroscopy (Perkin Elmer 4100) at 766.5 nm (K) and 852.1 nm (Cs) using LaCl$_3$ to control the ionization. K was chosen as a test cation because its relative selectivity compared to H^{+} is only 2.5, which means that if K^{+} is totally extracted in these experimental conditions, all the other cations of interest (Cs, Mn, Fe, Co, Sr, Be, Pb) will also be extracted, because they have higher relative selectivity (Table 1).

Table 1
Relative selectivity for cationic exchange on strongly acidic resin (AG 50W).

Cation	Relative selectivity	Cation	Relative selectivity
H^{+}	1.0	Fe^{3+}	2.55
Na^{+}	1.5	Co^{2+}	2.8
K^{+}	2.5	Ni^{2+}	3.0
Cs^{+}	2.7	Sr^{2+}	4.95
Mn^{2+}	2.35	Pb^{2+}	7.5

γ-Spectrometry was carried out with an ENERTEC (Schlumberger) high purity type p spectrometer (16 % relative efficiency; resolution at 122 and 1332 keV of 0.89 keV and 1.82 keV respectively). Data treatment was carried out with the software Interwinner. The spectrometer was calibrated using a gel containing a mixture of ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{85}Sr, ^{113}Sn, ^{88}Y. No absorption corrections were made for the resin measurements, the density of which was close to the density of the gel and contained essentially ^{12}C and ^{16}O atoms. Uncertainties are calculated following the law of propagation of uncertainties with counting statistics and γ-counting efficiencies uncertainties as the major sources of combined uncertainties. Detection limit for γ-spectrometry in this paper is based mostly on the background contribution to the signal and on the counting time, as well as efficiency for a given γ-line. LD is then calculated following Currie's law, assuming a coverage factor at 2σ.

2.1. Experimental design

Fig. 1 displays the main features of the collecting and extracting device. The cylindrical housing of the rainwater collector, including a heating unit for sampling snow, was left unchanged and a cylindrical container (the cartridge) with a diameter of 47 mm containing 80 g of resin (Dowex 88) was fitted into the end of the funnel. The resin inside the container is held by two polyamide grids (0.4 mm). Details of its geometry are given in Fig. 1 and construction plan can be obtained from the corresponding author. This box can be taken off by the operator of the collecting station, capped at both ends and sent to the laboratory. The resin and grids are replaced after each use. The 80 g of the resin from the cartridge and the particles on top of the upper grid are homogenized and transferred to our calibrated geometry (D5, 6.5 cm diameter, 24 mm height) for gamma spectrometry. Surprisingly, the most significant drawback of the method is the dirt (leaves, needles etc.) in the rainwater which can obstruct the grid. Therefore, using a large diameter filter is essential in order to prevent clogging of the filter after only a few liters of rainwater have passed through. A volume meter can be fitted to the outlet behind the cartridge to allow for rainwater volume determination, letting results to be given in Bq L^{-1}.

3. Results and discussion

Preliminary tests of the resin were carried out using stable alkaline cations (K and Cs) because ^{137}Cs will be one of the major radionuclide sought after in the event of accidental release from a nuclear power plant. Tests were made by gravity, which leads to a high elution rate (40 l per hour at a slightly acid pH of 5) to simulate an episode of heavy rainfall. Virtually all the K and Cs were retained in the resin and we concluded from these tests that the geometry of the cartridge and the type of resin result in a rapid exchange rate suitable for collecting rainwater.

It is not easy to simulate rainwater containing radioactive contamination. This is because of the presence of particles and most likely the majority of radioactivity is particle-borne in rainwater. Therefore, we decided to use water from the cooling system of nuclear reactors, which contains radionuclides like ^{54}Mn, ^{60}Co, and ^{65}Zn resulting from activation of materials. Usually part of the activity is of particulate form due to the corrosion of the cooling system. γ-spectrometry was carried out before and after the water passed through the cartridge. Another fraction of the contaminated water was filtered at 0.20 μm to remove particles. This water was also passed through the cartridge in order to evidence the role of particle-borne radioactivity in the extraction yields. Results are presented in Table 1 and show that only about 10–20% of the nuclides (^{60}Co, ^{58}Co, ^{54}Mn, ^{137}Cs and ^{65}Zn) are not retained by the resin in unfiltered water. In filtered water the trapping efficiency for all measured nuclides is 100% with the possible exception of ^{65}Zn. This result combined with the slightly lower extraction efficiency for particle-containing water shows that the system can detect radionuclides with satisfactory efficiency. We observed that the resin acts partly as a filter for the coarser particles but also that the strongly acidic resin can exchange H^{+} for radioactive cations adsorbed on smaller sized particles (Table 2).

In one experiment we wanted to compare both methods (evaporation and resin) at one site (Fribourg collecting site) in order to demonstrate the differences in the measurement of strongly adsorbing elements like ^{7}Be. Two identical rain sampler funnels
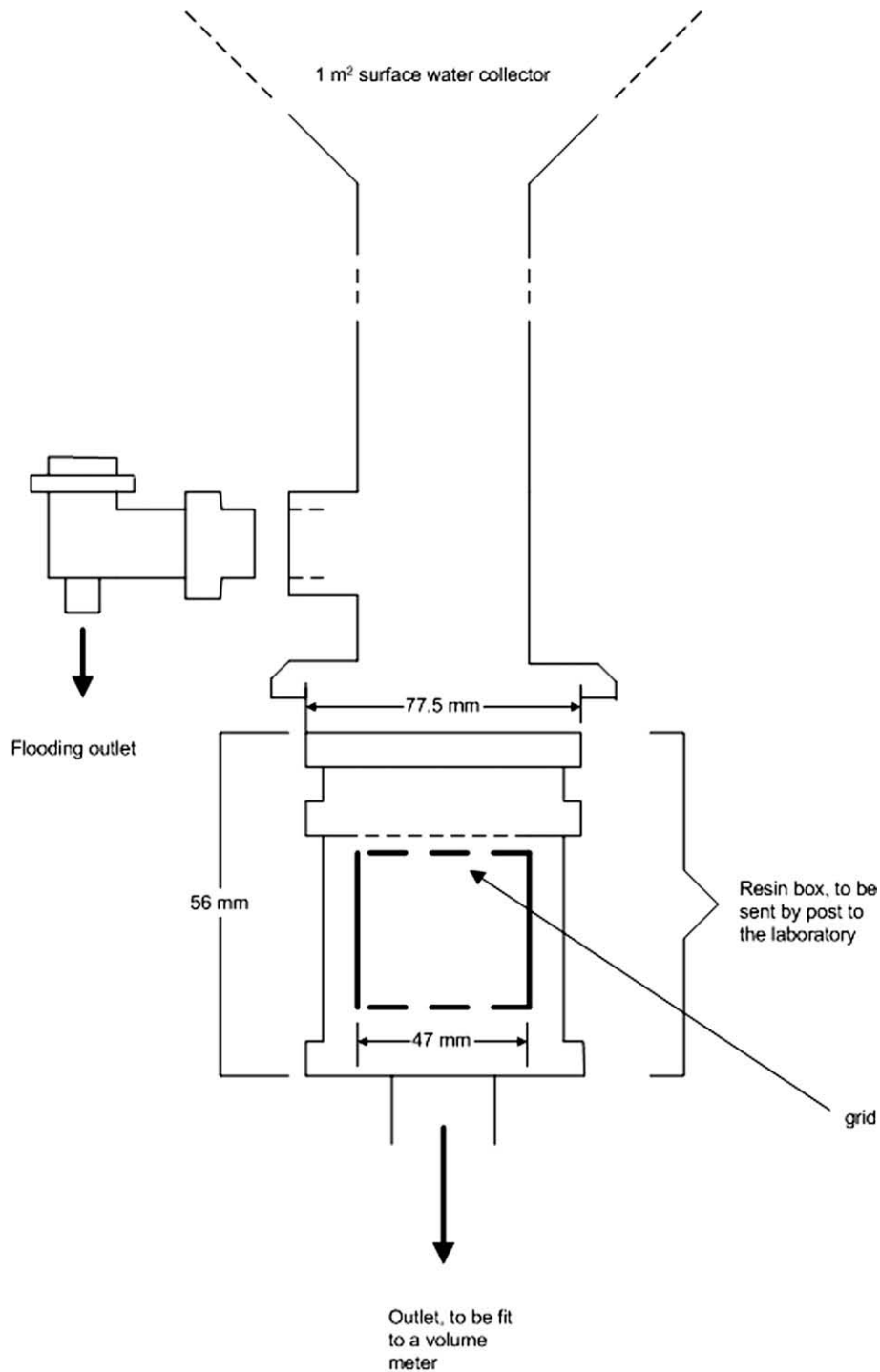
Fig. 1. Schema of the apparatus. Rainwater collected in the funnel is directed to the resin box. The flooding outlet is aimed to remove water in the collector in case the resin becomes clogged. The resin box can be clamped by two covers before sending to the laboratory. The top grid is designed to contain the resin and to remove the coarser particles of dust, needles, dead insects and leaves, etc.

placed on the roof of the Institute of Physics of the University of Fribourg collected the rainwater during the same period (December 2005). One of the collectors was connected to the resin system while the water collected in the second one was evaporated before γ-spectrometry. The concentrations of ^{7}Be obtained by the two methods differ significantly. The evaporation method gave an activity of 221 mBq L^{-1} while the resin method resulted in an

activity of 750 mBq L^{-1}. It seems that during evaporation two thirds of the activity can be lost. This occurs by aerosol formation during evaporation and/or by adsorption on the evaporation device walls, in spite of a careful washing of the evaporation system with 10% formic acid.

Even if ^{7}Be is not the main radionuclide sought in an environmental radioactivity survey program, its measurement in rainwater

Table 2
Percentage of radionuclides extracted on the resin in experiments where water from nuclear power plant cooling systems were either filtered or unfiltered.

	^{54}Mn	^{58}Co	^{60}Co	^{65}Zn	^{137}Cs
% Under particulate form >0.2 μm	22	23	49	55	6
% Extracted in the resin (unfiltered)	83 ± 9	90 ± 28	64 ± 5[a]	–	76 ± 45
% Extracted in the resin (unfiltered)	87 ± 7[b]	96[c]	82 ± 10[b]	79[c]	91[c]
% Extracted in the resin (filtered)	101 ± 4	96 ± 6	98 ± 3	78 ± 19	101 ± 5

[a] This low value might be due to the effect of particles settling in the measurement of ^{60}Co in the reference bottle.

[b] 100% will be the sum of the activities measured in the resin and in the solution that passed through the resin, in which activity was still measurable.

[c] Based on the detection limit of each radionuclide in the solution after having passed through the resin.

Table 3
^{22}Na/^{7}Be ratio in air and rainwater at different locations in the world.

Location	^{22}Na/^{7}Be (air)	^{22}Na/^{7}Be (rainwater)	Reference
Japan		1.9×10^{-4}	Komura et al., 2007
Japan		1.6×10^{-4}	Komura et al., 2006
Braunschweig (Germany)	2.0×10^{-4}		Jasiulionis and Wershofen, 2005
Güttingen (Switzerland)	$1.5 \pm 0.5 \times 10^{-4}$	$2.4 \pm 1.4 \times 10^{-4}$	This work

gives some interesting features of atmospheric deposition and air re-loading after a rainfall event. In fact, ^{7}Be, being of cosmic origin, allows for the study of air circulation and stratosphere–troposphere mixing as well as meteorological variables (Blaauboer and Smetsers, 1997; Caillet et al., 2001; Alonso-Hernàndez et al., 2004; Measday and Ho, 2004). After a rainfall event, Caillet et al. (2001) determined an air re-loading time of 1–2 days based on ^{210}Pb and ^{7}Be determination in rainwater. Since ^{7}Be is always measurable in rainwater, it can be used as an internal standard of atmospheric deposition as well as for checking the efficiency of a collecting device, the chemical preparation of the sample and the spectrometry measurement chain. Fig. 2 displays the results of ^{210}Pb and ^{7}Be determination in rainwater using the resin method in order to compare with the ratio obtained in the measurement of ^{210}Pb/^{7}Be ratio in air filters collected at different places in Switzerland and the data from Caillet et al. (2001) obtained after iron hydroxide precipitation. We can see that the different methods give a similar ratio, or at least within an interval that might be reasonable considering the different origin of both radionuclides and the large uncertainties of the ratio, mainly due to very low counting rate. Moreover, Caillet et al. (2001) show enhanced ^{210}Pb activities during periods of low precipitation, possibly due to enhanced ^{222}Rn emanation in dry weather, followed by important scavenging of ^{210}Pb in reduced rainfall rate events. This phenomenon will yield higher ^{210}Pb/^{7}Be than usual. Nevertheless, for the quality control of our new method of determining radioactivity in rainwater, the results displayed in Fig. 2 confirm that the resin technique gives a similar ratio to other methods with practically no treatment of the sample.
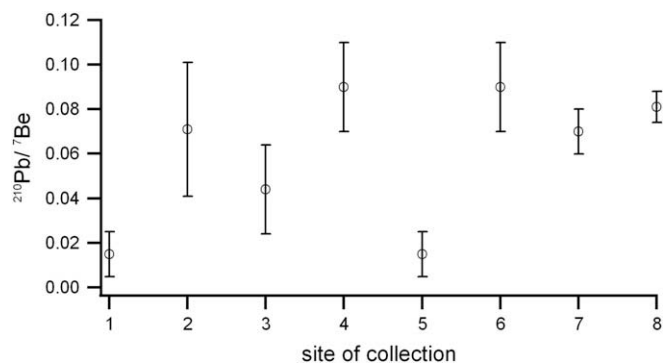
In one occasion we measured ^{22}Na above the detection limit. This was because 150 l of rainwater has passed through the resin. ^{22}Na/^{7}Be ratio was within the range expected for ^{22}Na/^{7}Be in rainwater as compared to values from Germany and Japan (Table 3). Thus, as a consequence of the much larger volumes that the resin method allows to analyzed compared to the evaporation method, cosmogenic radionuclide with low production rate, such as ^{22}Na, can be detected.

Finally, the main radionuclide that we wanted to measure in rainwater was ^{137}Cs. With the former evaporation method, ^{137}Cs was not detectable, probably due to the fact that only a few liters of rainwater were collected in the bottle before over-flooding. In principle, with the resin method there is no limitation of the volume of water that can be passed through the cartridge. Consequently, more radioactivity is collected and is therefore detectable. The results in Fig. 3 show that ^{137}Cs can be measured in rainwater with the resin method (0.1 Bq per sample) and the ratio ^{137}Cs/^{7}Be is comparable to those measured on air filters.

Additionally but out of the scope of this study, cations can be release from strongly acidic resins by 5 M HCl. Afterwards classical radiochemical procedures can be applied to determine radionuclides such as plutonium, americium and ^{90}Sr. On the other hand selective elution directly from the Dowex resin using EDTA and CyDTA complexing agents can be used to separate actinides from ^{90}Sr as described in Froidevaux et al., 2006. To get a better detection limit, the resin from different collecting periods can be mixed together before the elution of the cations.
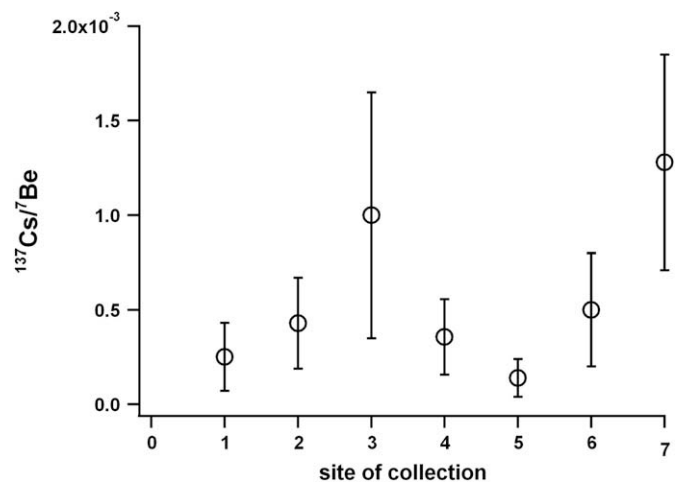
Fig. 2. Comparison of ^{210}Pb/^{7}Be ratio measured in rainwater events at Fribourg collecting station (1: 02.10.06; 2: 14.11.06; 3: 24.10.07), in rainwater near Mühleberg nuclear power plant (point 8). and in air filters collected during the year 2006 at Gösgen nuclear power plant (point 4), Leibstadt nuclear power plants (point 5) Fribourg (point 6) and in rainwater near Geneva, data from Caillet et al. (2001) (point 7).

Fig. 3. Comparison of ^{137}Cs/^{7}Be ratio measured in rainwater events at Fribourg collecting station (1: 02.10.06; 2: 14.11.06; 3: 16.07.07; 4: 24.10.07), Mühleberg nuclear power plant (point 7) and in air filters collected during the year 2006 at Fribourg (point 5) and near the Swiss nuclear power plants (point 6).

4. Conclusions

A simple modification of otherwise classic large surface rain-water collectors to incorporate a cartridge containing strongly acidic resin allows the quantitative extraction of radioactivity (as a cation) in rainwater. Even in the event of heavy rainfall the resin is able to cope with a high elution rate (40 l per h) and the only drawback of the method is linked to the clogging of the resin by dust, dead leaves and insects that might accumulate in the collector during a stormy period. The resin acts as a filter for large particles and extracts radioactive cations from smaller particles and from solution. In future research, we intend to test a combination of cationic and anionic exchange resins in order to include the determination of ^{131}I, a radioelement readily dispersed into the atmosphere following an accidental release as Komura et al. (2007) demonstrated for atmospheric chlorine isotopes. On the other hand the resin method allows the analysis of large rainwater volumes which led to the detection of ^{137}Cs, ^{210}Pb, ^{7}Be and ^{22}Na. All these radionuclides are of major importance for scientist studying atmospheric processes.

Acknowledgement

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