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Factors controlling ^{7}Be and ^{210}Pb atmospheric deposition as revealed by sampling individual rain events in the region of Geneva, Switzerland

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Abstract

Bulk atmospheric deposition of ^{7}Be and ^{210}Pb has been measured at Versoix, close to Geneva, Switzerland. Collectors were continuously deployed from November 1997 through November 1998 for periods from 1 to 22 days depending on the frequency of rain. The activities of ^{7}Be and ^{210}Pb integrated over the sampling interval were moderately well correlated with rainfall (r^2 of 0.66 and 0.55, respectively; $p<0.001$) and well correlated one with the other (r^2 of 0.91; $p<0.001$). The $^{7}Be/^{210}Pb$ activity ratio is close to 13.5, except for samples collected in the periods of very low precipitation which have a distinctly lower ratio. A simple model accounting for rainfall, seasonal variations and reload of the local atmosphere after a rain event explains 90% of the variance of ^{7}Be and ^{210}Pb deposition. Concentrations of ^{210}Pb and Ca^{++} in rain were correlated with transport time of air masses over the continent as indicated by reconstruction of air mass trajectories over three days.

Keywords: ^{7}Be; ^{210}Pb; Rain; Precipitation; Atmosphere; Deposition

1. Introduction

The natural radionuclides ^{7}Be and ^{210}Pb have found numerous applications in studies of transport processes in atmospheric and aquatic systems. ^{7}Be is a cosmogenic radionuclide produced in atmosphere by spallation of oxygen and

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nitrogen by high-energy cosmic-ray particles. It is removed from the atmosphere by radioactive decay (half-life 53.2 days) and by wet and dry deposition. The mean tropospheric residence time is estimated at between 22 and 48 days (Bleichrodt, 1978; Durana, Chudy & Masarik, 1996). The global ^{7}Be distribution has been described and modelled (Brost, Fleicher & Heimann, 1991; Koch and Mann, 1996).

Most of the ^{210}Pb in the atmosphere is formed as a decay product of ^{222}Rn emanating from soil. Early applications of ^{210}Pb as a tracer of atmospheric processes have been reviewed by Robbins (1978). Somewhat conflicting residence times of ^{210}Pb in the troposphere ranging from days to one month have been reported, depending on the method used, but the detailed study by Tokieda, Yamanaka, Harada and Tsunogai (1996) confirms the relatively short residence time of tropospheric aerosols carrying ^{210}Pb (4.8 ± 0.3 days). Preiss, Melieres and Pourchet (1996) compiled most of the surface air concentrations and atmospheric fluxes available in the literature.

Although the data-base of ^{7}Be and ^{210}Pb atmospheric deposition is growing, mainly due to routine monitoring programmes of radioactive fallout, the factors inducing temporal variability of atmospheric fluxes at a given location are not quite fully understood. In the majority of studies, a moderate correlation between radionuclide fluxes and rainfall is observed, whereby generally higher correlation coefficients are found for ^{7}Be than for ^{210}Pb (Olsen et al., 1985; Schuler et al., 1991). In contrast, the correlation between ^{7}Be and ^{210}Pb fluxes at the same location is generally good (Baskaran, Coleman & Santschi, 1993) in spite of the different origins of these radionuclides.

The goal of this study is to evaluate the importance of factors which, apart from rainfall, influence the removal of ^{7}Be and ^{210}Pb from the atmosphere. To this purpose, sampling after individual rain events was undertaken. We demonstrate here that the season and time elapsed between consecutive rain events significantly affect the magnitude of deposition of both radionuclides.

2. Materials and methods

Atmospheric traps collecting bulk deposition were installed from November 1997 to November 1998 at the Institute F.-A. Forel, located in Versoix (N46°16′28″-E6°10′16″), 10 km east of Geneva. They were placed on top of a mast, 3 m above the ground, to avoid, as much as possible, any soil-derived contribution. The sampling station is located on a jetty and the land near the lake shore is covered with grass. In a number of samples, ^{210}Po was measured. The ^{210}Po/^{210}Pb ratio was close to 0.1, indicating that direct re-suspension of soil particles was not a problem, at least for the samples examined. The sampling site is located at an altitude of 372 m; the annual average rainfall is 1000 mm. Prevailing wind directions are from the NE, bringing generally dry air, and from the W, bringing maritime, humid air.

The first trap consisted of a cylindrical polyethylene jar with a surface area of 0.275 m^2 (capacity 200 l). Samples were collected after each individual precipitation event and the trap replaced. Three litres of 1.5 N HNO_3 were poured into the trap

prior to each deployment in order to prevent adsorption of radionuclides on the jar wall. Stable Pb and Be (4 and 0.1 mg, respectively) were also added as tracers for checking the overall recovery. These quantities of stable metals were always in large excess over those expected from atmospheric input.

After exposure, the collector was emptied and rinsed with deionised water. This washing solution was then added to the sample. The largest particles were removed by filtration on a paper filter (Schleicher and Schuell). Stable and radioactive Be and Pb were concentrated by co-precipitation with Fe hydroxides similarly to the method described by Thompson and Turekian (1976) for seawater. Briefly, 0.55 mg of $FeCl_3$ was added per litre of sample, which had a $pH < 1$. After one day of equilibration, $Fe(OH)_3$ was precipitated by adding NH_4OH. This precipitate was removed by centrifugation, freeze-dried and dissolved in 40 ml of 1 N HCl.

The solution was transferred to a 250-ml gamma counting vial and measured in a closed-end high-purity Ge GMX coaxial detector (EG&G Ortec) coupled to an EG&G Ortec Spectrum Master 919 multichannel analyser. Energies at 46.5 keV and 477.7 keV were monitored for ^{210}Pb and ^{7}Be determination. Spectra were evaluated with the GammaVision™ software. Relative efficiencies were determined by measuring artificial standard solutions of ^{210}Pb and ^{7}Be isotopes exactly in the same conditions as the unknown samples. Typically, each solution was counted for 3–4 days to provide the lowest reasonable analytical error. ^{7}Be activities were corrected for decay to the time of deposition.

An aliquot of the sample was also measured by quadrupole-based ICP-MS (HP4500) for stable Pb and Be content. Their concentrations were measured with a typical precision of 2% and were used for the calculation of the overall recovery efficiency. Recoveries were fairly constant at $\sim$75–90% for both elements.

A second trap, for major element determination, was placed beside the 'radionuclide' jar and was retrieved at the same time. It consisted of a pre-cleaned polyethylene pot covered by a funnel with a surface of 0.047 m^2, except during winter when the funnel was removed because of the snowfall. At that time, the collecting surface area was reduced to 0.017 m^2. The samples were filtered through a 0.45 μm cellulose nitrate membrane and were divided in two parts: (i) 50 ml were acidified with 0.3% HNO_3, stored at 4°C, for further Ca^{++} and Na^{+} analysis carried out by AAS (Pye Unicam SP-9), (ii) 50 ml were stored at -30°C and Cl^{-} was measured with IC (Dionex DX 500). Both methods have a precision of about 5%.

Meteorological data were provided by the Swiss Meteorological Institute (SMI) from the closest station at Geneva airport, about 5 km away from the sampling site. Although this distance is short, significant discrepancies may occur, particularly during local storms. However, a comparison of rainfall amount from three stations, all located within 10 km of Geneva, has shown that the variability for one individual event generally did not exceed 10%. Three-D backward trajectories of air masses at the pressure 850 hPa over a period of 3 days, starting from the moment of the maximum rain intensity, were computed by the SMI. For each rain event the distance and the duration of air mass travel over the continent were evaluated.

3. Results

Samples from 46 rain events were collected from November 3, 1997 to November 2, 1998. The total (wet and dry) integrated activities of ^{7}Be and ^{210}Pb deposited during the exposure time from 1 to 22 days (avg : 8 days), expressed in Bq m^{-2}, are reported in Table 1. The concentrations of ^{7}Be, ^{210}Pb, Ca^{++}, Na^{+} and Cl^{-} were obtained by dividing the total amount of element deposited during exposure by the amount of precipitation measured at Geneva airport (Table 1). The integrated activities of each individual event varied widely from 0.5 to 12.6 Bq m^{-2} for ^{210}Pb and from 1.6 to 177 Bq m^{-2} for ^{7}Be. At the same time, precipitation varied between 0.2 and 66.4 mm. From these data, annual fluxes of 150 ± 3 Bq m^{-2} y^{-1} for ^{210}Pb and 2087 ± 23 Bq m^{-2} y^{-1} for ^{7}Be were calculated, values comparable to those already reported for Switzerland, i.e. 108, 138 and 153 Bq m^{-2} y^{-1} for ^{210}Pb, and 2250, 2660 and 2760 Bq m^{-2} y^{-1} for ^{7}Be (Dominik, Schuler & Santchi, 1987; Schuler et al., 1991; Vogler, Jung & Mangini, (1996).

The concentrations of individual events varied from 0.06 to 3.30 Bq l^{-1} for ^{210}Pb and from 0.93 to 10.45 Bq l^{-1} for ^{7}Be. However, some events, corresponding to low rainfall (<5 mm), were characterised by significantly higher ^{7}Be and ^{210}Pb activities. Concentrations varying between 0.07 and 1.16 mg l^{-1}, 0.07 and 0.65 mg l^{-1} and 0.09 and 2.48 mg l^{-1} were observed for Cl^{-}, Na^{+} and Ca^{++}, respectively.

3.1. Seasonal pattern

After monthly averaging, higher means of radionuclide concentrations appeared in June, July and August. Application of the student's *t*-test indicated that the differences between this group of samples and the others are significant at a probability greater than 99%. No such trends were noticed for the major element concentrations.

4. Discussion

4.1. Relationship between the amount of individual precipitation and radionuclide activities

The integrated activities by event of ^{210}Pb and ^{7}Be are correlated with the magnitude of precipitation with correlation coefficients (r^2) of 0.55 and 0.66, respectively ($p<0.001$) (Fig. 1a,b). Such relationships have been commonly observed and explained by the fact that rainfall constitutes the major depositional pathway of these radionuclides (Turekian, Benninger & Dion 1983; Olsen et al., 1985). As previously observed, correlation of rainfall with ^{7}Be seems better than with ^{210}Pb (Olsen et al., 1985), likely due to a relatively greater contribution of ^{210}Pb from dry deposition. Some scattering of data points along the regression line could be the result of other processes. A close examination of the diagrams shows that two categories of samples can be distinguished. In the first category are the samples

having high ^{210}Pb and ^{7}Be activities with respect to precipitation. This category consists of precipitation events occurring in late spring and summer. Indeed, maximum ^{7}Be fluxes were generally measured during the same period (Turekian et al., 1983; Olsen et al., 1985; Baskaran et al., 1993) and were attributed to an intrusion of stratospheric ^{7}Be-rich air masses into the troposphere, when mid-latitude folding of the tropopause enhances stratospheric–tropospheric exchange (Young, Wogman, Thomas & Perkine, 1970; Viezee and Singh, 1980; Dutkiewicz and Husain, 1985). A seasonal trend of ^{210}Pb was also reported and explained by the emanation of ^{222}Rn from soils, which can be partly controlled by moisture (Olsen et al., 1985; Schuler et al., 1991). Warming up of frozen and snow-covered soils, as well as drying out of water-saturated soils may be of importance here, because of the abundance of high-altitude mountains in Switzerland. Tokieda et al. (1996) suggested that in spring a significant fraction of ^{210}Pb may originate from the higher atmosphere (probably the stratosphere) and that the deposition rate of ^{7}Be is correlated with the upper atmospheric component of ^{210}Pb. If this is the case also at the Geneva location, a part of the enhanced deposition of ^{210}Pb in the summer months might be attributed to this source.

Another category of samples exhibits lower radionuclide activities than expected (filled black circles, Fig. 1). To a rough approximation, this category groups the rains which promptly followed (by about 1 day or less) a previous rain period. As shown by Fig. 1c, the relation ^{210}Pb vs. ^{7}Be integrated activities exhibits a better correlation ($r^2 = 0.91$, $p < 0.001$) than precipitation vs. ^{210}Pb or ^{7}Be. This suggests that the deposition of both radionuclides is essentially governed by the same processes, confirming the observation of Baskaran et al. (1993). Actually, the parameters independent of the amount of precipitation seem to have similar effects on deposition of both radionuclides.

4.2. Relationship between the amount of precipitation and radionuclide specific concentrations

Ishikawa, Murakami, Skine and Yoshihara (1995) modelled the ^{7}Be concentrations in rain through time, $C(t)$, by the following function:

$$C(t) = a\mathrm{e}^{-kt} + b, \tag{1}$$

where a, k and b are constants, and t is time. Two different processes operate in a rainfall event. The exponential term is preponderant when t is small. It illustrates the scavenging of the radionuclides associated with the aerosols present below the clouds (washout) and dominates at the beginning of the rain. Conversely, the constant term becomes preponderant when t increases. At that time, the scavenging occurring inside the cloud during the nucleation process (rainout) governs the deposition.

In our data, the highest concentrations of ^{7}Be and ^{210}Pb were observed for low rainfall (group A on Fig. 2(a) and (b)). With increasing precipitation, the concentrations quickly decreased to $\sim$0.1–0.3 Bq l^{-1} for ^{210}Pb and to 1–4 Bq l^{-1} for ^{7}Be (group B). Obviously, this behaviour cannot be directly modelled by Eq. (1) because (i) the samples represent an integrated record over all the duration of the

Table 1
Radionuclide and major element data. Major elements are given with an error of ±5%, while errors of integrated activities, concentrations and $^{7}Be/^{210}Pb$ are given at the 66% confidence level

Date of collection	Exp.[a] (day)	Precip.[b] (mm)	^{210}Pb		^{7}Be		$^{7}Be/^{210}Pb$	Cl^- (mg l^{-1})	Na^+ (mg l^{-1})	Ca^{++}
			Integrated activity (Bq m^{-2})	Specific conc. (Bq l^{-1})	Integrated activity (Bq m^{-2})	Specific conc. (Bq l^{-1})				
Nov 7, 97	4	13	2.0 ± 0.2	0.16 ± 0.02	20 ± 1	1.6 ± 0.2	10 ± 1	0.60	0.49	0.58
Nov 14, 97	7	63	6.3 ± 0.6	0.10 ± 0.01	89 ± 5	1.4 ± 0.2	14 ± 2	0.51	0.33	0.15
Nov 21, 97	7	10	2.2 ± 0.3	0.22 ± 0.03	23 ± 1	2.3 ± 0.3	10 ± 1	0.57	0.37	0.59
Dec 4, 97	13	25	2.5 ± 0.3	0.10 ± 0.02	28 ± 2	1.1 ± 0.1	12 ± 2	0.29	0.24	0.31
Dec 16, 97	12	27	3.4 ± 0.4	0.13 ± 0.02	60 ± 2	2.2 ± 0.2	18 ± 2	0.68	0.41	0.56
Dec 31, 97	15	46	3.8 ± 0.4	0.08 ± 0.01	78 ± 2	1.7 ± 0.2	20 ± 2	0.35	0.22	0.65
Jan 8, 98	8	39	6.6 ± 0.6	0.17 ± 0.02	88 ± 3	2.3 ± 0.2	13 ± 1	0.79	0.49	0.44
Jan 15, 98	7	3	1.7 ± 0.2	0.57 ± 0.10	15 ± 1	5.0 ± 0.6	9 ± 1	1.16	0.62	1.44
Jan 23, 98	8	46	2.8 ± 0.4	0.06 ± 0.01	44 ± 2	1.0 ± 0.1	16 ± 2	0.31	0.16	0.43
Feb 4, 98	12	0.2	0.7 ± 0.3	3.30 ± 1.17	2 ± 1	7 ± 1	2 ± 1	NM[c]	NM	NM
Feb 9, 98	5	0.2	0.6 ± 0.2	2.99 ± 1.07	2 ± 1	10 ± 2	4 ± 2	NM	NM	NM
Feb 24, 98	15	14	2.5 ± 0.3	0.17 ± 0.03	19 ± 1	1.3 ± 0.1	8 ± 1	0.32	0.30	0.89
Mar 3, 98	7	0.2	0.6 ± 0.2	2.79 ± 0.73	2 ± 1	9 ± 2	3 ± 2	NM	NM	NM
Mar 5, 98	2	3	2.6 ± 0.4	0.84 ± 0.14	26 ± 1	8.3 ± 0.9	10 ± 1	0.91	0.53	1.94
Mar 10, 98	5	13	2.4 ± 0.4	0.19 ± 0.03	28 ± 1	2.2 ± 0.2	12 ± 2	0.73	0.47	0.38
Mar 16, 98	6	5	1.3 ± 0.3	0.25 ± 0.07	9 ± 1	1.7 ± 0.2	7 ± 2	0.22	0.14	0.81
Apr 6, 98	21	31	5.8 ± 0.5	0.19 ± 0.02	66 ± 3	2.2 ± 0.2	11 ± 1	0.24	0.29	0.91
Apr 9, 98	3	18	1.6 ± 0.2	0.09 ± 0.02	40 ± 3	2.2 ± 0.3	26 ± 4	0.11	0.08	0.25
Apr 20, 98	11	50	4.3 ± 0.6	0.09 ± 0.01	83 ± 5	1.7 ± 0.2	19 ± 3	0.22	0.13	0.26
Apr 21, 98	1	1	0.5 ± 0.1	0.48 ± 0.09	6 ± 1	5.5 ± 0.7	12 ± 2	0.94	0.52	1.48
Apr 29, 98	8	16	3.4 ± 0.3	0.22 ± 0.03	41 ± 2	2.7 ± 0.3	12 ± 1	0.29	0.19	0.59
May 7, 98	8	6	0.7 ± 0.1	0.13 ± 0.02	6 ± 1	1.2 ± 0.2	9 ± 2	1.06	0.65	0.81
May 29, 98	22	18	3.4 ± 0.4	0.18 ± 0.03	35 ± 2	1.9 ± 0.2	10 ± 2	0.64	0.47	0.62
Jun 2, 98	4	2	0.9 ± 0.2	0.44 ± 0.09	9 ± 1	4.1 ± 0.5	9 ± 2	0.82	0.42	1.71
Jun 5, 98	3	19	5.5 ± 0.6	0.29 ± 0.05	79 ± 4	4.2 ± 0.5	14 ± 2	0.43	0.28	0.62
Jun 8, 98	3	7	1.6 ± 0.2	0.23 ± 0.03	25 ± 1	3.6 ± 0.4	16 ± 2	0.40	0.40	0.98

Jun 13, 98	5	36	5.0 ± 0.6	0.14 ± 0.02	95 ± 7	2.7 ± 0.3	19 ± 3	0.56	0.40	0.45
Jun 17, 98	4	8	1.2 ± 0.1	0.14 ± 0.02	25 ± 1	3.0 ± 0.3	22 ± 3	0.97	0.53	0.64
Jul 6, 98	19	56	13 ± 2	0.22 ± 0.03	180 ± 10	3.1 ± 0.4	14 ± 2	0.26	0.30	0.89
Jul 9, 98	3	12	2.7 ± 0.3	0.24 ± 0.04	42 ± 2	3.6 ± 0.4	15 ± 2	0.18	0.17	0.97
Jul 14, 98	5	4	2.0 ± 0.2	0.45 ± 0.07	26 ± 1	5.8 ± 0.6	13 ± 2	0.64	0.58	1.49
Aug 4, 98	21	34	9.7 ± 0.9	0.29 ± 0.04	150 ± 7	4.4 ± 0.5	16 ± 2	0.31	0.34	1.05
Aug 13, 98	9	7	5.1 ± 0.5	0.77 ± 0.11	50 ± 3	7.6 ± 0.9	10 ± 1	0.60	0.35	1.89
Aug 26, 98	13	10	4.6 ± 0.5	0.47 ± 0.07	45 ± 2	4.6 ± 0.5	10 ± 1	0.68	0.62	1.05
Sep 4, 98	9	4	2.2 ± 0.2	0.52 ± 0.08	19 ± 1	4.3 ± 0.5	8 ± 1	0.89	0.59	2.48
Sep 7, 98	3	54	4.0 ± 0.5	0.07 ± 0.01	67 ± 3	1.2 ± 0.1	17 ± 2	0.34	0.21	0.23
Sep 15, 98	8	66	9.8 ± 1.0	0.15 ± 0.02	118 ± 5	1.8 ± 0.2	12 ± 1	0.27	0.21	0.24
Sep 18, 98	3	5	0.5 ± 0.1	0.10 ± 0.02	8 ± 1	1.5 ± 0.2	14 ± 3	0.48	0.39	0.27
Sep 29, 98	11	21	4.3 ± 0.5	0.20 ± 0.03	66 ± 5	3.1 ± 0.4	15 ± 2	0.35	0.27	0.45
Oct 1, 98	2	30	1.7 ± 0.2	0.06 ± 0.01	28 ± 1	0.9 ± 0.1	16 ± 2	0.21	0.14	0.17
Oct 5, 98	4	16	1.8 ± 0.2	0.11 ± 0.02	34 ± 3	2.1 ± 0.3	19 ± 3	0.23	0.12	0.12
Oct 8, 98	3	18	1.8 ± 0.2	0.10 ± 0.02	36 ± 2	2.0 ± 0.2	20 ± 3	0.08	0.07	0.09
Oct 13, 98	5	5	1.0 ± 0.2	0.19 ± 0.04	13 ± 1	2.5 ± 0.3	13 ± 3	0.54	0.24	0.49
Oct 20, 98	7	10	1.0 ± 0.1	0.10 ± 0.02	15 ± 1	1.5 ± 0.2	14 ± 2	0.07	0.11	0.48
Oct 27, 98	7	53	6.0 ± 0.7	0.12 ± 0.02	92 ± 7	1.8 ± 0.2	15 ± 2	0.51	0.35	0.13
Nov 2, 98	6	41	3.6 ± 0.4	0.09 ± 0.01	63 ± 3	1.5 ± 0.2	18 ± 2	0.57	0.44	0.21

[a] exposure time.
[b] precipitation (error ± 10%).
[c] NM: not measured.

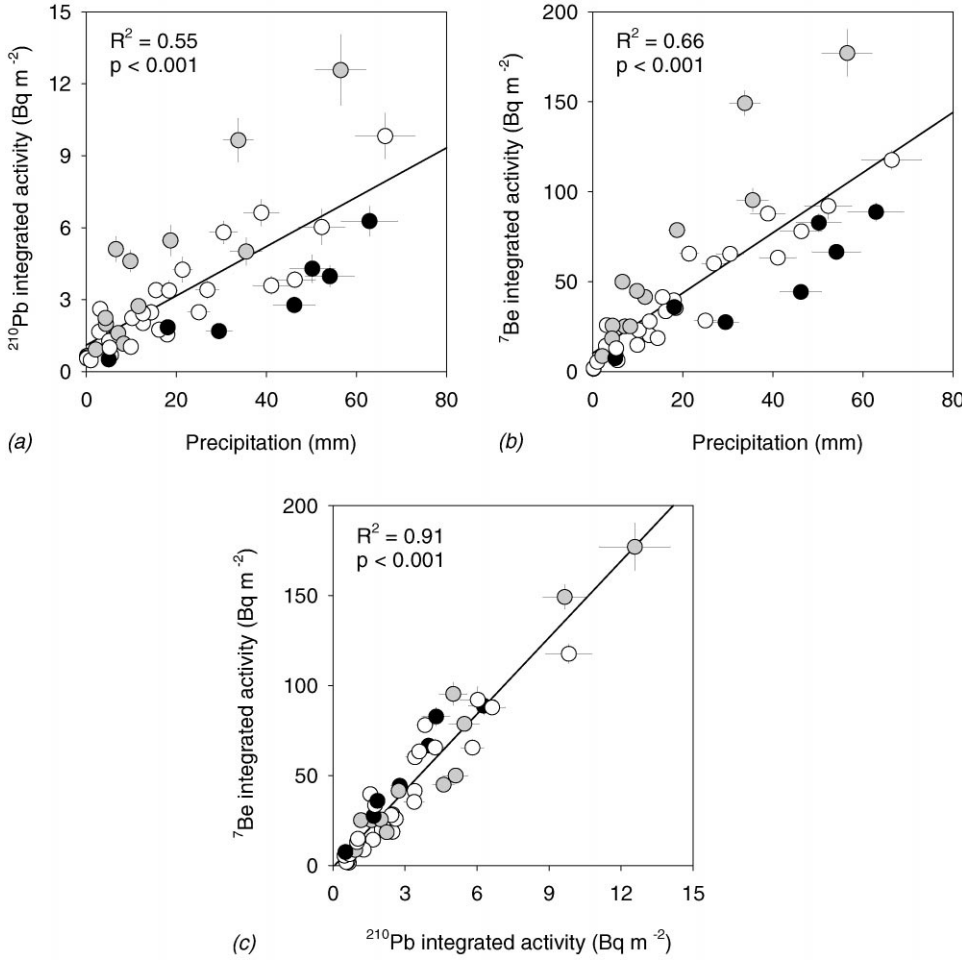

Fig. 1. (a) Precipitation vs. ^{210}Pb integrated activities, (b) precipitation vs. ^{7}Be integrated activities and (c) ^{210}Pb integrated activities vs. ^{7}Be integrated activities for 46 individual rain events. Black filled circles: rain events for which the delay between the sampled event and the preceding rain did not exceed one day; grey filled circles: rain events sampled between early June and August; and open circles: remaining events.

rain and, (ii) they include dry fallout. Nonetheless, the high concentrations observed in low rainfall (group A) likely illustrate the preponderance of washout and/or possibly a significant contribution of dry deposition. With heavier rainfall, the lower atmosphere is quickly washed and the relative importance of washout against rainout becomes negligible (group B). The range of ^{210}Pb and ^{7}Be concentrations is then narrower, despite some variations which will be discussed later.

^{210}Pb and ^{7}Be concentrations are plotted against each other in Fig. 3. Most of the samples belonging to group B fall on a line which defines a ^{7}Be/^{210}Pb ratio of about 13.5. No significant seasonal variations in the ^{7}Be/^{210}Pb ratios were found, despite

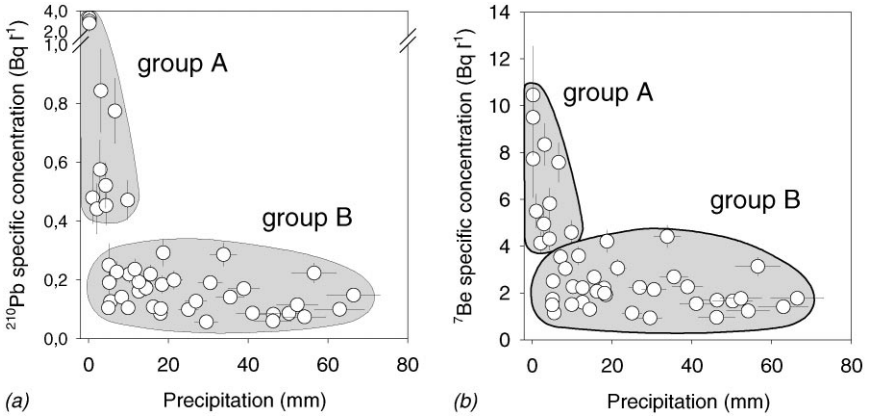

Fig. 2. (a) Magnitude of precipitation vs. ^{210}Pb concentrations and (b) magnitude of precipitation vs. ^{7}Be concentrations for 46 individual rain events. Highest concentrations for low rainfall (group A); with increasing precipitation, the concentrations quickly decrease (group B).

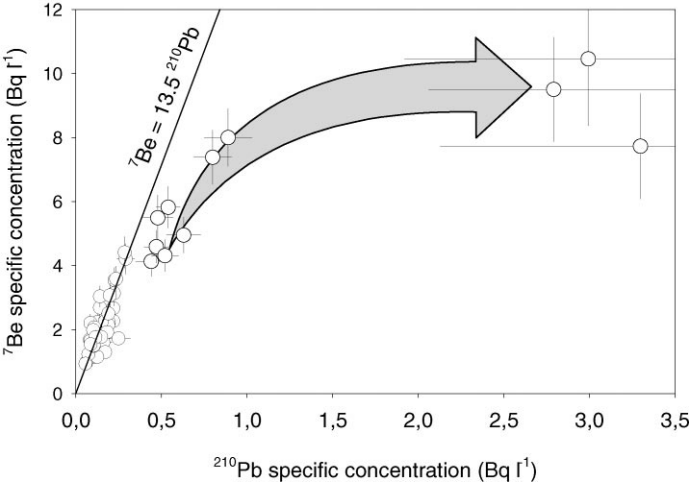

Fig. 3. ^{210}Pb concentrations vs. ^{7}Be concentrations for 46 individual rain events. The regression line (^{7}Be = 13.5^{210}Pb) has been computed from samples belonging to group B (high rainfall). The grey arrow indicates the deviation (to an enrichment of ^{210}Pb) when the precipitation is lower.

an increase of concentrations of both radioisotopes in late spring and summer. When the precipitation becomes lower, an enrichment of ^{210}Pb is observed (grey arrow on Fig. 3). This is particularly evident for the lowest precipitation (<1 mm), which show ^{7}Be/^{210}Pb ratios of about 3. This behaviour may be interpreted as a relatively important contribution of ^{210}Pb-rich, soil-derived particles, because not all samples were measured for their ^{210}Po/^{210}Pb ratios. Moreover, the washout and dry deposition could proportionally remove more ^{210}Pb than ^{7}Be because of a difference

in their vertical distributions in the lower atmosphere (Moore, Poet & Martell, 1973; Talpos and Cuculeanu, 1997).

4.3. Model of ^{210}Pb and ^{7}Be deposition

Based on the above relationships, we have attempted to model the radionuclide fallout during a single event as a function of the amount of precipitation, season and elapsed time between two rain events. The same depositional processes can reasonably be assumed for both ^{7}Be and ^{210}Pb, although differences between the nuclides have been identified at the lowest levels of precipitation. Nonetheless, these do not play any significant role in terms of flux. As illustrated by Fig. 1(a) and (b), most of the variance of ^{7}Be and ^{210}Pb deposition is due to the amount of precipitation and can be expressed by a linear law proposed by Ishikawa et al. (1995) and derived from Eq. (1)

$$A_i(P) = a_i + b_i P, \tag{2}$$

where $A_i(P)$ is the activity of radionuclide i deposited per m^2 during the exposure time, and P is the amount of precipitation. In this relation, $A_i(P)$ is the result of a linear combination of a term proportional to the precipitation ($b_i P$), which expresses the rainout, and an independent term (a_i). This latter represents the contribution of washout and dry deposition; however, a contribution, even minor, by soil-derived particles cannot be totally excluded. It is reasonable to assume that the coefficients a_i and b_i depend on the radionuclide inputs in the atmosphere.

Therefore, a_i and b_i are affected by the seasonal variability and the reload process of the atmosphere. This can be expressed by the following equations:

$$a_i = f_{\mathrm{Si}}\, f_{\mathrm{Ri}}\, a_{0i}, \tag{3}$$

$$b_i = f_{\mathrm{Si}}\, f_{\mathrm{Ri}}\, b_{0i}, \tag{4}$$

where f_{Si} is a function which describes the seasonal variability, f_{Ri} illustrates the reload process, whereas a_{0i} and b_{0i} are constants, for the radionuclide i. As suggested by the concentration data, a step function (f_{Si}) was used:

$$f_{\mathrm{Si}} = \begin{cases} d_i & \text{in June, July and August,} \\ 1 & \text{otherwise,} \end{cases} \tag{5}$$

where the input of nuclide i in the atmosphere is d_i times higher in June, July and August.

A Lagrangian model has been used to describe the reload process. We have assumed that the local atmosphere is uniformly mixed and the meteorological situation is representative of air masses on a large scale. The radionuclides are supposed to be completely scavenged after a rain event and the reload is approximated by an exponential function f_{Ri}:

$$f_{\mathrm{Ri}} = (1 - \mathrm{e}^{-k_i t}), \tag{6}$$

where t is the time which separates two rain events and k_i is the reload rate.

Although the reload concept is somewhat intuitive, it can be compared to a reload of the atmosphere with aerosol particles as described by Bergametti, Dutot, Buat-Menard, Lasno and Remoudaki (1989). Both large and local scale processes can be involved here. As inferred from backward air mass trajectories, most of the meteorological fronts bringing precipitation to Geneva come from the west, 'cleaning' the atmosphere from radionuclides over considerable distances. If two precipitation events closely follow one another, the advective transport of air masses may be not fast enough to completely recharge the atmosphere on the same trajectory. On the local scale, Geneva is surrounded by the Jura mountains and the Alps, with periodically stagnant air masses (temperature inversion) which may slow down the recharge of the lower troposphere by advective transport, resulting in a lower radionuclide inventory being available for washout when the time between two rain events is short.

From all the above, the activity of radionuclide i (A_i) deposited per m^2 during the exposure time is given by:

$$A_i = \begin{cases} d_i(1 - e^{-k_i t})(a_{0i} + b_{0i}P) & \text{in June, July and August,} \\ (1 - e^{-k_i t})(a_{0i} + b_{0i}P) & \text{otherwise,} \end{cases} \quad (7)$$

Multiple regressions have been computed for ^{210}Pb and ^{7}Be data. The resulting values of the coefficients are reported in Table 2. Both seasonal and reload functions were significant at more than 99.9% according to a Fisher F-test. The activities calculated by the model for ^{7}Be and ^{210}Pb were very similar to the measured values, as shown in the Fig. 4(c) and (d). Regression coefficients ($r^2 = 0.86$ for ^{210}Pb, and $r^2 = 0.92$ for ^{7}Be, Fig. 4(c) and (d) were much better than those calculated when only the precipitation was included ($r^2 = 0.55$ for ^{210}Pb and 0.66 for ^{7}Be, Fig. 4(a) and (b). A greater part of the variance is thus explained by considering the seasonal and reload functions. Moreover, such high coefficients close to unity undoubtedly argue in favour of the mathematical formulations chosen to model the natural processes which enrich or deplete the atmosphere.

The values of d indicate an increase by $68 \pm 9\%$ and $80 \pm 9\%$ of the ^{210}Pb and ^{7}Be inputs, respectively, in June, July and August. The synchronicity and these similar amplitudes of the increases for both radionuclides are maybe fortuitous. As a matter of fact, if the increase of the ^{7}Be concentration is generally observed worldwide at the same latitudes, it is evident that the concentration of ^{210}Pb is highly dependent on climate, geographical situation and the nature of the underlying rocks. As a

Table 2
Coefficients d, k, a_0 and b_0 determined by multiple regressions. Errors are given at the 66% confidence level

	d	k (d^{-1})	a_0 (Bq m^{-2})	b_0 (Bq l^{-1})
^{210}Pb	1.68 ± 0.09	0.80 ± 0.08	0.9 ± 0.1	0.12 ± 0.01
^{7}Be	1.80 ± 0.08	0.96 ± 0.10	6.3 ± 1.1	1.74 ± 0.06

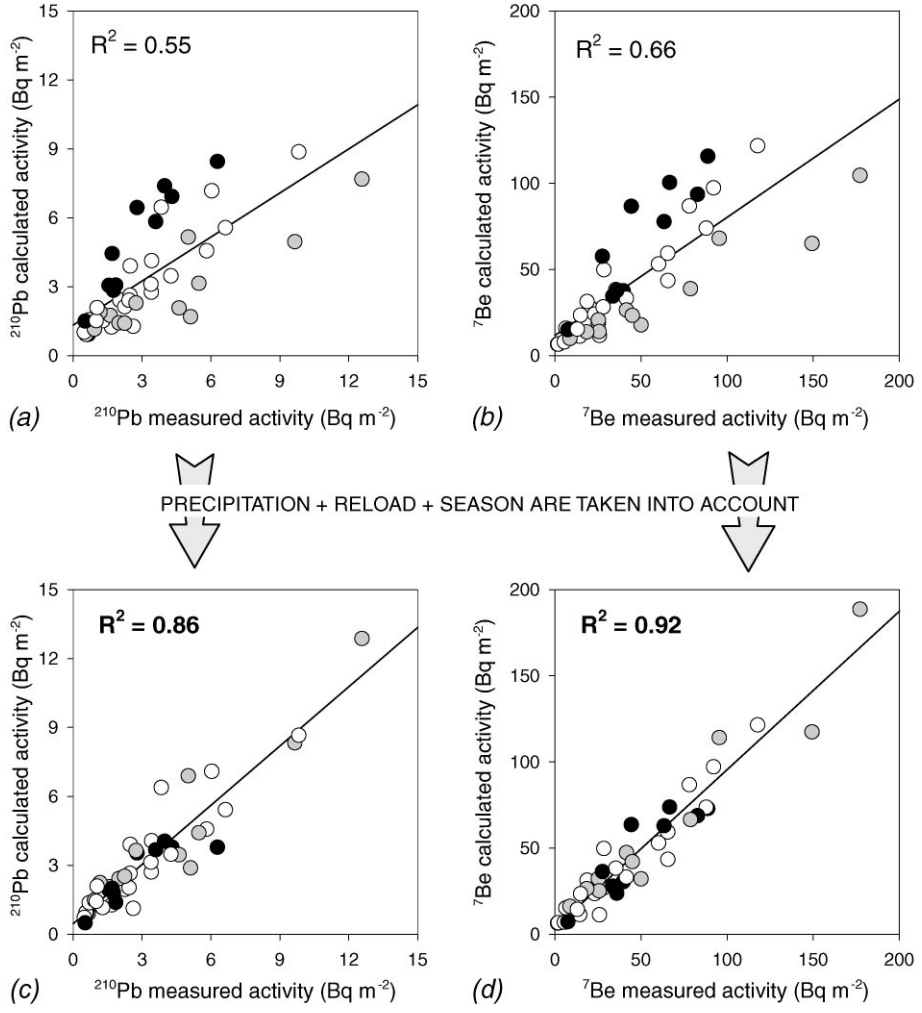

Fig. 4. Measured vs. integrated activities calculated with a linear model taking into account the precipitation alone (Eq. (2)) for ^{210}Pb (a) and for ^{7}Be (b); and with a model where both seasonal and reload process are also included for ^{210}Pb (c) and for ^{7}Be (d). Black filled circles: rain events for which the delay between the sampled event and the preceding rain did not exceed one day; grey filled circles: rain events sampled between early June and August; and open circles: remaining events.

consequence, what is true in the region of Geneva may be quite different in other parts of the world. Nevertheless, the simultaneous enhancement of ^{210}Pb and ^{7}Be from the upper troposphere and from the stratosphere in spring is also possible (Tokieda et al., 1996).

The parameter k allows us roughly to assess the mean time necessary to reload the atmosphere with radioisotopes ($t_r = 1/k$). Values of 1.2 ± 0.1 day and 1.0 ± 0.1 day are calculated for ^{210}Pb and ^{7}Be, respectively. As the production rate and the origin

of both elements are quite different, it is impossible to invoke a common reload process governed by emissions alone. The local atmosphere would rather be reloaded by a rapid mixing with surrounding air masses. In this case, it is normal to find very similar ^{210}Pb and ^{7}Be (and other element) reload times. This is in good agreement with the average reload time of 2 days for aerosol particles from continental sources (Bergametti et al., 1989).

The constant a_{0i} corresponds to the contribution from washout and dry deposition in a rain event not affected by seasonal variability or partial reload. By extrapolation over the whole year, this contribution represented $27 \pm 3\%$ and $16 \pm 3\%$ of the total deposition of ^{210}Pb and ^{7}Be, respectively. This is consistent with the fact that washout and dry deposition are more important for ^{210}Pb than for ^{7}Be.

Finally, b_{0i} gives an estimation of the mean ^{210}Pb and ^{7}Be concentrations in a rain event dominated by the rainout process and is not affected by seasonal variability or by partial reload.

4.4. ^{7}Be, ^{210}Pb and origin of air masses

Two tools were used to assess the origin of air masses: backward trajectory via meteorological observations and more indirectly the measurement of major element concentrations (Cl^-, Na^+ and Ca^{++}). In the following, the samples largely dominated by the washout mechanism (group A as defined in Fig. 2) should be dropped because their high concentrations are not related to long-distance transport of air masses.

When Ca^{++} and ^{210}Pb concentrations are plotted vs. the duration of air mass travel over the continent (Fig. 5), two groups of samples are distinguished. The first

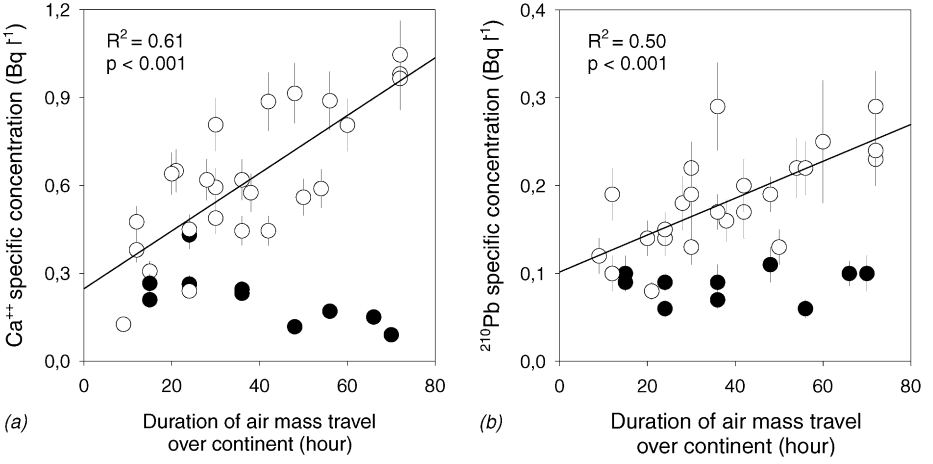

Fig. 5. Duration of air mass travel over continent vs. Ca^{++} (a) and vs. ^{210}Pb (b) concentrations. Rain events largely dominated by washout (group A in Fig. 2) are excluded. Black filled circles: rain events for which the delay between the sampled event and the preceding rain did not exceed one day, and open circles: the others.

one presents an evident correlation ($r^2 = 0.61$ for Ca^{++} and $r^2 = 0.50$ for ^{210}Pb), suggesting that Ca^{++} and ^{210}Pb are progressively incorporated into the air masses during travel over the continent. The second group is characterised by low Ca^{++} and ^{210}Pb concentrations, independently of the travel duration. These latter samples correspond to the events which quickly followed past rain events (one day or less), as defined above. As a result, ^{210}Pb and Ca^{++} concentrations show a fair correlation ($r^2 = 0.51$). Both elements originally come from soil and they seem to behave similarly in regard to the incorporation, transportation and fallout mechanisms from the atmosphere. Although systematically measured, the Na^+ and Cl^- concentrations, which can potentially be used as indicators of oceanic influence, did not exhibit inverse correlation with the ^{210}Pb concentrations, although this nuclide is essentially of continental origin. The maritime signal is possibly too weak and/or perturbed by local sources. ^7Be concentrations (not shown) appeared much less dependent on the air-mass travel time ($r^2 = 0.22$) than Ca^{++} and ^{210}Pb since it is not preferentially incorporated in the air masses over the continents.

5. Conclusions

Mean fluxes of 150 ± 3 Bq m^{-2} y^{-1} and 2087 ± 23 Bq m^{-2} y^{-1} were measured for ^{210}Pb and ^7Be, respectively. An examination of the individual rain event allowed definition of the main removal processes with respect to the amount of precipitation. Despite their different origins, the deposition of both radionuclides is essentially governed by the same processes. The high ^{210}Pb and ^7Be specific concentrations observed at low rainfall illustrate the preponderance of washout and/or a significant contribution of dry deposition. With heavier rainfall, the lower atmosphere is quickly washed out and the rainout process dominates.

From these findings, a simple depositional model was developed. It takes into account the amount of precipitation, the season and the elapsed time between two rain events. Accounting for 60% of the flux variance, the amount of precipitation is the main factor. From the end of spring and during summer, the concentrations of both radionuclides in the rain increase by 70–80%. This is ascribed to intrusion of stratospheric air masses into the troposphere and to a greater emanation of ^{222}Rn from snow-free and dry soils. After a rain event, the mean reload time of the atmosphere for both radionuclides was estimated at 1–2 days. The model describes the atmospheric fluxes fairly well by explaining about 90% of the variance during the sampling period.

The inter-relationship between air mass trajectories and the concentrations of ^{210}Pb and Ca^{++} illustrates the common continental origin of these elements. Given its cosmogenic origin, ^7Be does not show any particular trend compared to the major element concentrations and the trajectories.

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