# What can gross alpha/beta activities tell about 210Po and 210Pb in the atmosphere?

Luca Terray, Donato D Amico, Olivier Masson, Jean-Christophe Sabroux

Journal of Environmental Radioactivity

# What can gross alpha/beta activities tell about 210Po and 210Pb in the atmosphere?

**Luca Terray** : *Laboratoire Magmas et Volcans, Université Clermont Auvergne, Aubière, France Et Laboratoire de Physique de Clermont, Université Clermont Auvergne, Aubière, France*

**Donato D'Amico**, **Olivier Masson** et **Jean-Christophe Sabroux** : *Institut de Radioprotection et de Sûreté Nucléaire (IRSN), Fontenay-aux-Roses, France*

**What can gross alpha/beta activities tell about $^{210}$Po and $^{210}$Pb in the atmosphere?**

**Abstract:** $^{210}$Po and $^{210}$Pb represent the most abundant part of atmospheric aerosol long-lived natural radioactivity. Moreover, $^{210}$Pb-$^{210}$Po monitoring in the atmosphere can be of interest for tracking extreme natural events that can enhance the level of alpha/beta radioactivity in air. In this paper, we question the possibility to use routine gross alpha/beta measurements in order to monitor $^{210}$Po, $^{210}$Pb and $^{210}$Po/$^{210}$Pb ratio in the atmosphere. Based on joint gross alpha/beta measurement and $^{210}$Pb-$^{210}$Po specific determination on 16 atmosphere samples, we show that (i) gross beta activity systematically overestimates $^{210}$Pb activity due to the presence of interfering beta emitters and (ii) gross alpha activity mostly reflects $^{210}$Po activity even if an underestimation is always observed due to alpha particle attenuation. In order to determine $^{210}$Po/$^{210}$Pb ratio, we discuss the advantages of using gross alpha activity time variation compared to specific $^{210}$Po measurements. Finally, the gross alpha/beta ratio appear to be a good proxy of the $^{210}$Po/$^{210}$Pb ratio when large-scale variations are to be monitored. We report a first reference level for the activity level of airborne $^{210}$Po in France of 13 ± 6 µBq/m$^3$.

## 1. Introduction

Long-lived radon daughters (namely $^{210}$Pb, $^{210}$Bi and $^{210}$Po) are widely used in atmospheric studies (see recent reviews by Baskaran, 2011, 2016). These radionuclides can be considered as tracers, as well as chronometers of air mass circulation. They are also useful to determine the residence time and the removal rate of aerosols in the atmosphere. In addition, they play a major role in the monitoring of atmospheric radioactivity because they are responsible for the most part of long-lived (> 5 days) natural radioactivity of atmospheric aerosols (see figure 1 and compilation in “Sources and effects of ionizing radiation", UNSCEAR 2008 Report, 2010). Therefore, the levels of long-lived radon daughters and their natural variability mostly influence reference levels and alert thresholds in the atmospheric radioactivity monitoring and early warning context.

Extreme natural events such as volcanic eruptions, forest fires or dust resuspension events are known to release important quantities of radioactive $^{210}$Po into the atmosphere (*e.g.* Lambert et al., 1982; Le Cloarec et al., 1995; Nho et al., 1996). For instance, Allard et al. (2016) recently reported that Ambrym volcano (Vanuatu) is continuously emitting $^{210}$Po into the atmosphere at a rate of 210 TBq/year. In comparison, the estimated amount of polonium released during the October, 1957 Windscale accident is 42 TBq (Garland and Wakeford, 2007), which is to say only a fifth of the Ambrym cumulative emission in one year. Moreover, such natural discharge episodes are likely to happen regularly and in many places worldwide due to the important number of sources (either active volcanoes, burning biomass or deserts), thus potentially increasing the exposure of local population to ionizing radiations ($^{210}$Po is highly toxic when inhaled or ingested due to its very high specific activity

54 and emission of energetic alpha particles inside the body) and triggering anomalies of long-
55 lived alpha radioactivity in the atmosphere.

56 Consequently, it appears important for atmospheric radioactivity monitoring purposes
57 (including nuclear forensics) to be able to detect such events, which implies to discriminate
58 between natural and anthropogenic sources, and to assess the average background
59 concentration of airborne $^{210}$Po.

60 In this article, we investigate the possibility of determining atmospheric $^{210}$Po/$^{210}$Pb ratio
61 using gross alpha-beta activity measurements. Actually, both volcanic and forest fire plumes
62 are traced at long-distance by an increase in the $^{210}$Po/$^{210}$Pb ratio compared to background
63 atmospheric values (Nho et al., 1997; Paatero et al., 2009). Indeed, high temperature
64 natural processes favour the release of the more volatile element, polonium, as compared to
65 lead. Thus, $^{210}$Po/$^{210}$Pb ratio is a relevant clue to attribute an increase of atmospheric
66 radioactivity to an extreme natural event such as a volcanic eruption or a forest fire.
67 However, the specific measurement of $^{210}$Po and $^{210}$Pb at environmental levels requires
68 either a long analysis on a very sensitive Germanium detector ($^{210}$Pb) or a long and
69 destructive chemical process ($^{210}$Po) prior to radioactive counting. Therefore, a routine
70 monitoring of $^{210}$Pb and $^{210}$Po of atmospheric aerosols requires an important technical
71 support and is not easy to set up and maintain from the operational point of view.
72 Contrastingly, gross alpha/beta activity measurements are easier to perform on a regular
73 basis. Even if alpha/beta counting instruments are only able to discriminate beta and alpha
74 particles and do not allow to infer the nature of the radionuclide, the technique has strong
75 advantages: first, it does not need any sample preparation (the filter can be directly placed
76 inside the counter) and second, alpha/beta counting devices can generally host many

77 samples. For these two reasons, this technique is widely used in the field of aerosol
78 radioactivity monitoring. As far as France is concerned, there is a very dense network of
79 nuclear power plants and other nuclear installations in France monitoring gross alpha/beta
80 air indices on a daily basis (this network is referred to as *Réseau National de Mesures de la*
81 *radioactivité de l'environnement*, see the RNM website in the references). Therefore, if
82 alpha/beta gross activity ratio is found to be well representative of the $^{210}Po/^{210}Pb$ ratio it
83 would then be possible to track the signature of extreme or at least unusual natural events
84 with a simple (and already widely operational) routine procedure.

85 On one hand, the correlation between $^{210}Pb$ and beta long-lived (>5 days) activities in
86 atmospheric aerosol samples has already been evidenced (Mattsson et al., 1996) suggesting
87 that $^{210}Pb$ is responsible for most of the beta long-lived activity. Nevertheless, the presence
88 of other beta emitters (like $^{40}K$, $^{32}P$ or $^{33}P$) in the atmosphere is well known (Lal and Suess,
89 1968; Lujanien et al., 1997; Schery, 2001; Hernández et al., 2005) and can occasionally reach
90 significant levels. Occurrence of positive anomalies of these beta emitters could depend on
91 several factors (such as the locality of the sampling point and the history of the air mass) and
92 we still have to understand precisely the conditions leading to significant gaps between $^{210}Pb$
93 and beta activity. On the other hand, the correlation between $^{210}Po$ and alpha activity has
94 never been clearly established (as far as we know) on an important series of samples. Even if
95 many individual measurements of the most naturally abundant alpha-emitters ($^{238}U$, $^{232}Th$,
96 $^{226}Ra$) systematically point negligible activities compared to $^{210}Po$, the outstanding
97 contributor of the alpha atmospheric radioactivity (see figure 1 and table 14 in "Sources and
98 effects of ionizing radiation", UNSCEAR 2008 Report,"2010), the validity of the
99 supposed correlation between $^{210}Po$ and gross alpha activities still needs to be evaluated.

In this study we collected a series of atmospheric aerosol samples and measured on the same aliquot (see methods hereafter) $^{210}Pb$, $^{210}Po$ and gross alpha/beta activities in order to examine jointly the two aforementioned correlations. This allows us to finally assess the constraints on $^{210}Po/^{210}Pb$ ratio provided by gross alpha/beta activity ratio.

## 2. Methods

### 2.1 Atmospheric sampling

Atmospheric aerosols have been sampled on the top of the building of the Observatoire de Physique du Globe de Clermont-Ferrand (OPGC) located in the Campus des Cézeaux (Aubière city, France) in the neighbourhood of Clermont-Ferrand city at an elevation of about 400 m. We used a MegaVol-3000 particulate air sampler from Ecotech that was operated at a flow rate of 150 $m^3/h$. Air was pumped through a polypropylene filter (3M) similar to the filters of OPERA-AIR network (see OPERA network website in the references) with a minimum collection efficiency of about 95% for particles with an aerodynamic diameter of 30 nm. The impacted area on the filter is a rectangle of 18 by 23 cm (414 $cm^2$).

Eleven samples were collected on a weekly basis between March and June 2017. Five more samples were collected between February and June 2018. Sampling durations range between 45 and 87 hours with a mean of 56 h, which is equivalent to a filtered air volume of 8,400 $m^3$. Starting time and sampling duration were decided in order to avoid important precipitation events and shifts of meteorological regimes during sampling.

Each filter was dried and weighted before and after sampling in order to measure the sampled mass of dry particulate matter. Sample details are provided in table 1.

## 2.2 Radioactivity analysis

Immediately after drying and weighting operations, a circular aliquot of 125 mm diameter was cut in the centre of the filter and sent to IRSN-SAME laboratories in Le Vésinet, France, for a set of analyses. SAME (Service d'Analyses et de Métrologie de l'Environnement) is the service of IRSN in charge of environmental radioactivity measurements. The following 3-steps protocol was applied to the first eleven samples (collected in 2017):

- **Step 1:** gross alpha/beta counting of the aliquot and $^{210}$Pb measurement by gamma spectrometry (with a germanium detector) as soon as it was received, approximately 5-10 days after sampling in order to get rid of the short-lived radon and thoron daughters (see figure 1). These analyses will be referred to as the 5-day analyses hereafter for convenience, even if some of them were not exactly performed 5 days after sampling (see table 1). 5-day gross alpha/beta counting is a typical measurement for most of atmospheric radioactivity monitoring systems and such measurements are commonly available in many places in France through a common sharing platform (see RNM website in the references).
- **Step 2:** Repetition of step 1 (gross alpha/beta counting and gamma spectrometry of the aliquot) 50 days after sampling, in order to reach the radioactive equilibrium between $^{210}$Bi and $^{210}$Pb ($^{210}$Bi is the daughter of $^{210}$Pb and has a half-life of 5.2 days as compared to the 22.2-year half-life of its parent). These analyses will be referred to as the 50-day analyses in the following. Such delayed analyses are rarely performed in the context of aerosol radioactivity monitoring but they present a significant interest when performed in addition to the 5-day

analyses. Indeed, this second set of measurements allows to make a direct comparison between $^{210}$Pb and gross beta activity. Actually, $^{210}$Pb can only be indirectly measured by the alpha/beta counter through the decay of its daughter $^{210}$Bi because the beta end-point energies of $^{210}$Pb are too low (i.e. $E_{max}$=17 and 63 keV) to produce detectable electrons, while $^{210}$Bi has a much higher beta end-point energy ($E_{max}$ = 1162 keV). After 50 days, $^{210}$Bi activity is equal to $^{210}$Pb activity and then any difference between gross beta activity and $^{210}$Pb activity is necessarily due to other radionuclides present in the filter.

- **Step 3:** specific measurement of $^{210}$Po by alpha spectrometry after mineralization of the aliquot, chemical separation of polonium and plating of polonium onto silver plates.

The same aliquot was systematically used for all analyses in order to avoid potential biases due to sample heterogeneity. For the five samples collected in 2018, the protocol was composed of steps 1 and 3, and step 3 started just after step 1 was completed in order to minimize $^{210}$Po build-up in the sample before the measurement by alpha spectrometry.

### 2.3 Meaning of gross alpha/beta activities

Detection yields of gross alpha/beta counting detectors have been determined using $^{90}$Sr-$^{90}$Y sources for beta and $^{239}$Pu for alpha. These sources have been produced by droplet deposition of radioactive standard liquid solutions on blank filters. The type and geometry of these filters were similar to those of samples in order to minimize calibration biases due to different geometries and matrices between calibration sources and measured filters. Accordingly, gross beta activity is expressed as equivalent $^{90}$Sr activity and gross alpha activity is expressed as equivalent $^{239}$Pu activity.

169 However, since different radionuclides emit particles (either beta electrons or alpha
170 particles) with different energies, the detection yield obtained with some radionuclides ($^{90}$Sr-
171 $^{90}$Y and $^{239}$Pu in our case) might not be representative of the detection yield for any other
172 radionuclide. In order to better interpret the results, some qualitative considerations can be
173 made. As far as gross alpha activity is concerned, it should be noted that $^{239}$Pu alpha particle
174 energies (5,105-5,156 keV) are close to $^{210}$Po alpha particle energy (5,304 keV). Therefore,
175 the <4% relative difference of initial alpha particle energy might have a negligible effect on
176 the detection yield since it is similar or even lower compared to typical alpha energy
177 resolution measured above air filters (full width at half maximum from a few hundred keV
178 up to 1 MeV according to Moore et al., 1993). However, mechanisms affecting alpha activity
179 measurements of air filters are numerous and complex to assess (*e.g.* Geryes et al., 2009)
180 and a bias on the yield could still arise from external factors such as the depth of
181 radionuclide entrapment in the filter, or alpha energy absorption by aerosol particles
182 accumulated in and on the filter.

183 Contrastingly, gross beta activity might rather underestimate the activity of most beta
184 natural emitters such as $^{210}$Bi, $^{40}$K, $^{33}$P, or $^{35}$S. This is because beta electrons from a $^{90}$Sr-$^{90}$Y
185 mix have higher energies (561.4 keV on average) compared to beta electrons coming from
186 $^{210}$Bi, $^{40}$K, $^{33}$P, or $^{35}$S (317, 508.32, 76.4, and 48.79 keV on average, respectively). On the
187 contrary, $^{32}$P emits beta electron with a mean energy of 695.5 keV and its activity could be
188 overestimated by the gross beta activity. However, this approach based on average beta
189 electron energy cannot be used for making quantitative bias assessments since it does not
190 take into account the geometry of the sample-detector ensemble and the shapes of energy
191 spectra at low energy where most of yield differences are rooted.

## 2.4 Correction of $^{210}$Po build-up in the filter

Since $^{210}$Pb has a 22.2 years half-life, it can be considered as stable during the whole sampling and analysis periods. This is not the case for $^{210}$Po due to its much shorter half-life of only 138.4 days. Because the time lag between sampling and $^{210}$Po analysis (typically 50-70 days) is not negligible compared to $^{210}$Po half-life, and because of the presence of $^{210}$Pb and $^{210}$Bi in the filter, $^{210}$Po can be regenerated (or eventually decay in the case of initial $^{210}$Po/$^{210}$Pb activity ratio greater than 1) in between the sampling time and the measurement time . Thus, a correction has to be applied in order to infer the activity of the filter at a given initial time prior to $^{210}$Po measurement (either sampling time, 5-day or 50-day analyses times). Since $^{210}$Po can be regenerated in the filter by the decay of his parent $^{210}$Bi, itself sustained by the decay of $^{210}$Pb, the correction depends on $^{210}$Pb, $^{210}$Bi and $^{210}$Po initial activities. The correction formula is given in appendix A. If necessary, the unknown $^{210}$Bi activity can be neglected (see appendix A).

## 2.5 Volume normalisation.

Atmospheric activities are finally calculated from the activities measured on the aliquot (and subsequently corrected for $^{210}$Po build-up), dividing by the volume of filtered air and the aliquot to filter surface ratio (this ratio is similar for all samples and is equal to 0.3). It is assumed that the analysed aliquot is representative of the whole filter.

## 2.6 Determination of $^{210}$Po/$^{210}$Pb activity ratio from gross alpha activity time variation

Two different approaches can be used to determine the $^{210}$Po/$^{210}$Pb activity ratio. The first method simply consists in dividing $^{210}$Po activity by $^{210}$Pb activity. It is independent from gross alpha/beta measurements but it implies a correction for $^{210}$Po (see section 2.4). Since this correction relies on the value of $^{210}$Pb activity determined by gamma spectrometry with

high uncertainty owing to low counting statistics, the corrected $^{210}$Po activity value at sampling time can be affected by important errors. An alternative method relies on the relative variation of gross alpha activity between 5-day and 50-day analyses and is based on the hypothesis that this variation is only related to $^{210}$Po variation inside the sample. This assumption will be discussed later in the light of obtained results. The correction formula is detailed in Appendix B.

## 3. Results

All measured atmospheric activities are reported in table 1 and plotted in figure 2. The uncertainty is given at a significance level of 2 sigma (95%) and only includes the uncertainty of the radioactivity measurements. Uncertainties on air volume and aliquot to filter ratio are small compared to the uncertainty due to counting statistics and calibration, and are thus neglected. What is more, errors related to the filtered volume or the aliquot to whole filter ratio do not propagate an error on activity ratios.

### 3.1 Gross alpha/beta and $^{210}$Pb activity levels

Gross alpha activity at 5 days was found at a level of 0.016 ± 0.008 mBq/m$^3$ (mean and standard deviation), and gross beta activity at 5 days was found at a level of 0.4 ± 0.2 mBq/m$^3$ (mean and standard deviation). These levels are consistent with the values usually reported in the RNM. $^{210}$Pb activity was found at a level of 0.3 ± 0.2 mBq/m$^3$, which is in good agreement with monthly averages previously recorded at sites located nearby our sampling site by Bourcier et al. (2011), *i.e.*, from 0.33 ± 0.10 mBq/m$^3$ to 1.13 ± 0.34 mBq/m$^3$ at the Opme station (5.7 km SSW from our sampling site), and from 0.34 ± 0.04 mBq/m$^3$ to 1.35 ± 0.14 mBq/m$^3$ at the Puy-de-Dôme observatory.

### 3.2 Gross beta activity versus $^{210}$Pb activity at 5 and 50 days and the excess of gross beta activity

Figure 3 displays 5-day beta activities as a function of $^{210}$Pb activities. A marked correlation between these two activities is found ($R^2$=0.98), but $^{210}$Pb activity is significantly lower than beta activity ($\beta$ = 1.27 × $^{210}$Pb + 0.05 mBq/m$^3$, best fit). At 50 days, a marked correlation between gross beta and $^{210}$Pb activities is also found ($\beta$ = 1.44 × $^{210}$Pb - 0.02 mBq/m$^3$, $R^2$ = 0.97). These excellent correlations at 5 and 50 days mean that $^{210}$Bi coming from $^{210}$Pb decay is the main source of long-lived beta radioactivity of atmospheric aerosols (*i.e.*, still present in the filter 5 days after sampling), in good agreement with previous studies (*e.g.*, Mattsson et al., 1996). However, obtained linear coefficients are significantly higher than 1 meaning that gross beta activity is in excess compared to $^{210}$Pb activity. As stated previously, gross beta activity might underestimate $^{210}$Bi activity and therefore this excess cannot be due to a calibration bias (if such a bias exists). At 5 days, $^{210}$Bi activity could be higher than $^{210}$Pb activity but this possibility can likely be discarded since $^{210}$Bi/$^{210}$Pb activity ratio is generally < 1 in tropospheric air with a typical value of 0.5 (Poet et al., 1972). Moreover, at 50 days, when $^{210}$Pb and $^{210}$Bi are in radioactive equilibrium, the clear discrepancy observed between gross beta and $^{210}$Pb activities proves that long-lived radionuclides different from $^{210}$Pb contribute to gross beta activity. Assuming that calibration biases can be neglected, it is thus possible to calculate the amount of beta radioactivity coming from those other sources. We find that the mean excess beta activity compared to $^{210}$Pb-$^{210}$Bi equilibrium activity is 0.1 mBq/m$^3$ (with a standard deviation of ± 0.1 mBq/m$^3$). Could such an excess be explained by the presence of other beta emitters like $^{40}$K, $^{32}$P, $^{33}$P, or $^{35}$S ? $^{40}$K activity was not detected by gamma spectrometry for any sample in this study and detection thresholds were typically higher than 0.1 mBq/m$^3$ (1.4 ± 0.7 mBq/m$^3$, mean and

standard deviation of detection thresholds). However, $^{40}K$ activity levels measured at the nearby Opme station (5.7 km SSW from our sampling site) (OPERA-AIR network) in the period March 2017-June 2018 are significantly lower than 0.1 mBq/m$^3$ with an average value of 6.2 ± 3.2 µBq/m$^3$ (Olivier Masson, unpublished data). Even if some episodic events with high $^{40}K$ atmospheric activities (Hernández et al., 2005) cannot be ruled out, these low-level measurements suggest that $^{40}K$ cannot be the main beta emitter contributing to the observed excess. $^{32}P$, $^{33}P$, and $^{35}S$ are pure beta emitters and therefore they cannot be measured by gamma spectrometry. However, the order of magnitude of airborne activity levels reported in the literature for $^{32}P$, $^{33}P$ and $^{35}S$ (Lal and Suess, 1968; Lujanien et al., 1997) is about 0.1 mBq/m$^3$. When summed up, the activities of cosmogenic radionuclides might exceed the observed excess of beta activity (~0.1 mBq/m$^3$). Nevertheless, the beta detection yield of $^{33}P$ and $^{35}S$ with a gross alpha/beta counting device might be very small due the low energy of electrons emitted by these nuclides (see section 2.3) and therefore only a minor part of their activity is accounted for in the measured gross beta activity. Thus, we suggest that the observed beta excess is compatible with a contribution of cosmogenic radionuclides.

### 3.3 Inferences on the gross beta activity excess from comparison between 5 and 50 days

Figure 4a represents gross beta activity at 5 and 50 days, as well as $^{210}Pb$ activity, for each of the 2017 samples. It can be observed that gross beta activity at 5 days is systematically higher than or similar to gross beta activity at 50 days. This observation is a further argument in favour of the contribution of cosmogenic radionuclides to the gross beta activity. Indeed, all the above-cited radionuclides have half-lives of a few tens of days: 14.3 days ($^{32}P$), 25.4 days ($^{33}P$) and 87.3 days ($^{35}S$). Therefore, their activity in the filter significantly decreases between 5 and 50 days.

In order to check whether the decrease of $^{32}P$, $^{33}P$ and $^{35}S$ is compatible with the observed decrease of gross beta activity, it is possible to calculate the apparent half-life of the gross beta activity excess (relative to $^{210}Pb$) using the following equation:

$$\tau_{app} = \frac{-\Delta t \ln 2}{\ln \frac{\beta_{50} - {}^{210}\mathrm{Pb}}{\beta_{5} - {}^{210}\mathrm{Pb}}}$$

(eq. 1)

where $\Delta t$ corresponds to the interval between 5-day and 50-day analyses and $\beta$ and $^{210}Pb$ correspond to gross beta activity and $^{210}Pb$ activity, respectively. This calculation is illustrated on figure 4b. Values of $\tau_{app}$ calculated for the ten samples acquired in 2017 range from 30 to 1500 days with a median value of 80 days and mean value of 271 days (one sample with lower gross beta activity at 5 days as compared to 50 days was excluded). Half of the computed values are higher than the expected half-lives. However, $\tau_{app}$ must be considered as a maximum estimate of the beta excess half-life since the increase in $^{210}Bi$ activity between 5 and 50 days could partially counter-balance the activity decrease of short-lived cosmogenic radionuclides. Indeed, $^{210}Bi$ activity is generally lower than $^{210}Pb$ in the troposphere (see above), therefore the activity of $^{210}Bi$ in the filter gradually increases until radioactive equilibrium is reached with $^{210}Pb$ after about one month.

Actually, two groups of samples can tentatively be separated: a six-sample group with a low apparent half-life (from 30 to 80 days, mean 50 days) associated to a significant gross beta activity decrease and a four-sample group with a high apparent half-life (from 160 to 1560 days, mean 680 days) corresponding with a barely significant decrease or lack of significant decrease. The first group might be composed of samples with higher $^{32}P$-$^{33}P$-$^{35}S$/$^{210}Pb$ activity ratios and/or a $^{210}Bi$/$^{210}Pb$ initial activity ratio closer to 1 (smaller $^{210}Bi$ build-up).

307 Alternatively, the second group 2 can be composed of samples with lower $^{32}P$-$^{33}P$-$^{35}S$/$^{210}Pb$
308 activity ratios and/or lower $^{210}Bi$/$^{210}Pb$ initial activity ratio (higher $^{210}Bi$ build-up).

309

310 3.4 Gross alpha activity versus $^{210}Po$ activity at 50 days

311 Figure 5 compares 50-day gross alpha activity and $^{210}Po$ activity. Reported polonium
312 activities are corrected for the build-up taking place between the gross alpha/beta counting
313 at 50 days and $^{210}Po$ measurement 10 to 20 days after (see methods for more details).
314 Uncertainties are calculated by quadratic propagation of $^{210}Po$ measurement uncertainty
315 and $^{210}Pb$ activity uncertainty (used for the correction, see appendix A). An excellent linear
316 correlation between the two activities is found ($R^2$= 0.99) and gross alpha activity at 50 days
317 is lower than $^{210}Po$ activity (best fit: $\alpha = 0.83 \times {}^{210}Po$ mBq/m$^3$, mean ratio of 0.72). Linear
318 correlation between the two activities strongly suggests that $^{210}Po$ is the main source of
319 alpha activity at 50 days. This is in agreement with previously reported activity levels of only
320 0.5-1 μBq/m$^3$ for long-lived alpha emitters in the atmosphere ($^{238}U$, $^{230}Th$, $^{226}Ra$, $^{232}Th$, $^{228}Ra$,
321 $^{228}Th$) ("Sources and effects of ionizing radiation", UNSCEAR 2008 Report, 2010 and
322 references therein). The fact that alpha gross alpha activity is smaller than $^{210}Po$ activity can
323 be explained by the measurement process and alpha particles self-absorption in the filter
324 (see discussion).

325 3.5 Gross alpha activity at 5 days versus build-up corrected $^{210}Po$ activity

326 Figure 6a represents gross alpha activity measured at 5 days as a function of build-up
327 corrected 5-day $^{210}Po$ activity (see methods). In marked contrast with the situation at 50
328 days, gross alpha and $^{210}Po$ activities are poorly correlated ($R^2$ = 0.77 for 2017 samples and
329 $R^2$ = 0.78 for 2018 samples), even though positive correlation trends are still observed.

Interestingly, even if correlation coefficients are similarly low for 2017 and 2018, the 2018 samples group (characterized by a shorter time lag before $^{210}$Po measurement) present a mean alpha/$^{210}$Po ratio closer to the mean ratio found for 50-day activities (5-day ratios of 0.66 for 2018 samples and 0.4 for 2017 samples, to be compared to the 50-day ratio of 0.72). Moreover, the uncertainty on build-up corrected $^{210}$Po activity is much higher for the 2017 sample group than for the 2018 sample group (see figure 6a). Since the 5-day alpha/$^{210}$Po ratio has no obvious reason to change between 2017 and 2018 and since $^{210}$Po is the outstanding contributor of long-lived alpha radioactivity (see figure 1), these observations suggest that the correction applied to $^{210}$Po activity in order to recalculate its value backward in time introduces an important dispersion and bias in the corrected values, especially when the correction lag is long (2017 sample group). Therefore, obtained $^{210}$Po corrected activities cannot be trusted as representative of $^{210}$Po atmospheric level for 2017 samples. Contrastingly, the good agreement between 5-day alpha/$^{210}$Po ratio of 2018 samples and the 50-day ratio suggests that corrected $^{210}$Po activities are not significantly biased.

### 3.6 Atmospheric $^{210}$Po/$^{210}$Pb activity ratio inferred from gross alpha activity variation (2017 samples)

Due to large uncertainty propagation on corrected $^{210}$Po activity using the $^{210}$Pb-based approach (see section 3.5), we attempted to determine $^{210}$Po/$^{210}$Pb activity ratio using the gross alpha activity variation method described in section 2.6. Results are presented in figure 7. This method relies on the assumption that the relative increase of gross alpha activity between 5 and 50 days is equal to the relative increase of $^{210}$Po activity in the filter. Conclusions drawn from section 3.4 confirm that long-lived alpha-emitting radionuclides found in the atmosphere (U, Th and Ra isotopes) are not active enough to invalid this

353 assumption (see also figure 1). Another source of uncertainty behind this method is the lack
354 of constraints on $^{210}Bi/^{210}Pb$ activity ratio in the filter. In order to evaluate the effect the
355 unknown $^{210}Bi/^{210}Pb$ activity ratio on this method, $^{210}Po/^{210}Pb$ activity ratio is calculated for
356 three different values of this parameter in equation B.4 (appendix B), i.e. 0, 0.5 and 1.

357 It is clear on figure 7 that the value of $^{210}Bi/^{210}Pb$ initial activity ratio has an effect on the
358 value of $^{210}Po/^{210}Pb$ activity ratio obtained from gross alpha activity variation (the higher the
359 assumed $^{210}Bi/^{210}Pb$ ratio, the lower the obtained initial $^{210}Po/^{210}Pb$ ratio). However, taking
360 into account uncertainties of gross alpha activity measurements, the results obtained with
361 different values of the $^{210}Bi/^{210}Pb$ ratio are not significantly different. Therefore, the effect of
362 $^{210}Bi$ can be neglected and we will consider afterward a mean value of 0.5 for $^{210}Bi/^{210}Pb$
363 ratio (Poet et al., 1972).

364 First, the obtained $^{210}Po/^{210}Pb$ ratio (0.07 ± 0.01, mean and standard deviation) is very close
365 to the 5-day gross alpha/$^{210}Pb$ activity ratio (0.06 ± 0.02). In comparison, the $^{210}Po/^{210}Pb$
366 mean ratio obtained from build-up corrected $^{210}Po$ activity is 0.18 ± 0.07. This shows that the
367 gross alpha activity variation method causes lower biases as compared to the $^{210}Po$ build-up
368 correction. Moreover, $^{210}Po/^{210}Pb$ activity ratios obtained with this method are in good
369 agreement with the mean atmospheric value of 0.06 previously reported by Daish et al.
370 (2005).

371 Using the same method, we computed the 5-day $^{210}Po/^{210}Pb$ ratio for each sample (taking
372 into account the exact time lag between sampling and 5-days analysis) and derived the 5-day
373 $^{210}Po$ activity (multiplying by $^{210}Pb$ activity) that we compared to 5-day gross alpha activity
374 (figure 6b). A much better correlation is found as compared to that of the other method ($R^2$=
375 0.95 versus 0.77). Moreover, the 5-day alpha/$^{210}Po$ ratio obtained with the gross alpha

activity variation method is in good agreement with the alpha/$^{210}$Po ratio found at 50 days. These results confirm that the alpha/$^{210}$Po ratio might not significantly change between 5 days and 50 days, and demonstrates that $^{210}$Po is the dominant long-lived alpha emitter of atmospheric aerosols.

### 3.7 Atmospheric $^{210}$Po/$^{210}$Pb activity ratio versus gross alpha/beta activity ratio

Figure 8 represents gross alpha/beta activity ratio measured at 5 days as a function of atmospheric $^{210}$Po/$^{210}$Pb activity ratio inferred from gross alpha activity variation (2017 samples) and from corrected $^{210}$Po activity (2018 samples). The two activity ratios are not well correlated ($R^2$ = 0.12 and 0.46 for 2017 and 2018 respectively). Gross alpha/beta activity ratio is lower than $^{210}$Po/$^{210}$Pb activity ratio by a mean factor of 0.9 (2017) or 0.6 (2018). Lower alpha/beta activity ratio as compared to $^{210}$Po/$^{210}$Pb activity ratio is logical since 5-day gross beta activity overestimates $^{210}$Pb activity (see section 3.2) and since alpha activity underestimate $^{210}$Po activity (see section 3.4). Thus, both differences tend to an underestimation of $^{210}$Po/$^{210}$Pb activity ratio by the alpha/beta activity ratio. However, it should be pointed out that both ratios are almost always compatible considering the large error bars, especially for the $^{210}$Po/$^{210}$Pb activity ratio. Actually, gross alpha/beta activity ratio has a typical relative uncertainty of 22% ± 14% (k=2) while $^{210}$Po/$^{210}$Pb ratios present larger relative uncertainties (36% ± 2% in 2018 and 50% ± 20% in 2017). For both kinds of ratio, the relative variability of the sample set (2σ standard deviation divided by mean) is not considerably higher than measurement uncertainties (48% for alpha/beta ratio and 70% for $^{210}$Po/$^{210}$Pb ratio).

### 3.8 $^{210}$Po levels in France

Based on the estimate of atmospheric $^{210}Po/^{210}Pb$ activity ratio and on measured $^{210}Pb$ activities, it is possible to determine the airborne $^{210}Po$ activity level at the study site. We find a level of $^{210}Po$ of 13 ± 6 µBq/m$^3$ (mean and standard deviation on all samples). This level is in very good agreement with levels reported in England by Daish et al., 2005 (12,3 ± 0,4 µBq/m$^3$) and constitutes the first chronicle of $^{210}Po$ activity in France.

## 4. Discussion

### 4.1 Origin and consequences of the gross beta activity excess compared to $^{210}Pb$

Gross beta activity is found in marked excess as compared to $^{210}Pb$ activity by a typical factor of ~1.3 (see section 3.2). This excess is higher at 5 days than at 50 days after sampling and can be attributed to the presence of short-lived cosmogenic radionuclides (see sections 3.2 and 3.3). This factor can serve as a correction factor to retrieve $^{210}Pb$ activity from 5-day gross beta activity. However, it is interesting to point out that a previous comparison study (based on a larger set of samples) did not identify this phenomenon (Mattsson et al., 1996). The authors found a regression equation equivalent to $\beta = 1.03 \times {}^{210}Pb + 0.02$ mBq/m$^3$ (see figure 9 in Mattsson et al., 1996) even if some samples could present a beta excess factor as large as 1.3. Even if a calibration bias cannot be ruled out, we suggest that the typical beta activity excess compared to $^{210}Pb$ (and the correction factor to apply) may depend on the location and on the potential presence of local sources of other beta emitters. As a consequence, the use of gross beta activity to infer $^{210}Pb$ activity might be cautious and requires a calibration of gross beta activity vs $^{210}Pb$ to be made on site, for instance using the protocol presented in this study. If such a calibration of gross beta activity vs $^{210}Pb$ activity

421 was performed on a large number of sampling stations, it would be possible to understand
422 how the excess of gross beta activity relates to environmental conditions.

423 In this study, the two gross beta activity has been measured only two times for each sample
424 (at 5 and 50 days). Yet, we have shown that gross beta activity likely reflects the presence of
425 several short-lived radionuclides including $^{210}$Pb-$^{210}$Bi, $^{32}$P, $^{33}$P and $^{35}$S. Thus, we suggest that
426 precise constraints on the nature of the beta excess could be obtained with at least 5 gross
427 beta activity measurements over a period of 50 days.

428 4.2 Alpha particles self-absorption in filters

429 The gross alpha activity has been found to slightly underestimate $^{210}$Po activity when
430 both activities are compared at 50 days. The cause of this difference likely lies in the
431 measurement process itself. Actually, measurement of alpha emitters in air filters is known
432 to be strongly biased by alpha particles attenuation inside aerosol particles and filter media
433 (Geryes et al., 2009 and references therein). Alpha particles interact efficiently with aerosol
434 particles and filter fibers and can possibly be stopped before reaching the detector which
435 causes a decrease in the gross detection efficiency. The correction of the alpha attenuation
436 in air filter consists in calibrating the alpha/beta counting apparatus with a filter
437 impregnated with a known amount of alpha radioactivity (see section 2.3). However, the
438 attenuation endured by alpha particles in the calibration filter can be slightly different from
439 the attenuation occurring in real atmospheric air filters. This could be explained, for
440 instance, because of different mechanisms of fixation (water droplets percolation versus
441 aerosols fixation) or because of attenuation caused by aerosol particles themselves. This
442 difference could result in a biased calibration coefficient. In the present case, we suggest
443 that alpha attenuation is slightly underestimated resulting in an underestimate of the gross

444 alpha activities by approximately 10% (see section 3.4). Therefore, in the context of
445 atmospheric radioactivity monitoring we recommend to calibrate alpha counting devices
446 using real aerosol filters in order to avoid potential matrix biases. The reference value of
447 alpha activity for calibration filters can be obtained via radiochemistry, as presented in this
448 study.

449

450 4.3 Advantages and disadvantages of $^{210}$Po measurement strategies in atmospheric
451 samples

452 Since $^{210}$Po is regenerated in the samples by $^{210}$Pb and $^{210}$Bi decays, precise measurement
453 of this radionuclide in the atmosphere is challenging. If $^{210}$Po is not measured within a few
454 days at most after sampling, its activity significantly increases in the sample which implies to
455 make a correction to retrieve the original $^{210}$Po content. Yet, this correction depends on
456 $^{210}$Pb which is difficult to estimate directly with high precision (since it requires long counting
457 times). Therefore, important errors can be made on the initial $^{210}$Po activity due to error
458 propagation and amplification from $^{210}$Pb measurement. Moreover, $^{210}$Bi activity is also
459 needed in the correction process, as variable $^{210}$Bi/$^{210}$Pb initial activity ratios will affect the
460 build-up of $^{210}$Po by $^{210}$Pb decay. This problem has also been investigated by Lozano et al.
461 (2011). Yet, precise measurement of $^{210}$Bi is also challenging since it is a pure beta emitter
462 mixed with other beta emitters in the filter. Its quantification would require either a
463 chemical separation or a continuous measurement of beta activity over a few weeks in order
464 to perform the proper deconvolution of the half-lives of the different beta emitters present
465 in the filter ($^{33}$P, $^{32}$P, $^{35}$S, $^{40}$K, $^{210}$Bi).

466 It has been shown that $^{210}$Po activity values corrected for build-up by $^{210}$Bi-$^{210}$Pb decay in the
467 filter in between 5 and 50 days are largely biased due to error propagation (see 3.5). This is
468 not surprising since this correction relies on $^{210}$Pb activity measured by gamma spectrometry
469 with high uncertainty (typical relative uncertainty of 30% in our study) and since any error on
470 $^{210}$Pb activity propagates to $^{210}$Po activity. Contrastingly, the same correction formula was
471 used for recalculating $^{210}$Po activity at 50 days (typical correction of 10-20 days, see table 1)
472 and did not introduce any notable dispersion (see section 3.4). The same observation stands
473 true for 2018 samples for which the time lag between 5-day alpha/beta counting and $^{210}$Po
474 measurement was 24 days at most . This suggests that the dispersion induced by the
475 correction is amplified as $^{210}$Po activity is recalculated sooner backward in time. Therefore,
476 precise $^{210}$Po specific activity determination implies a short time lag between sampling and
477 analysis (typically 10-20 days). If this condition is met, this technique has the major
478 advantage of being direct.

479 Another $^{210}$Po measurement strategy is based on $^{210}$Po/$^{210}$Pb ratio determination using gross
480 alpha activity variation with time. Compared to direct determination of $^{210}$Po, this method
481 has the main advantage to be simpler (no radiochemistry is needed). It is also worth to point
482 out that this method is not affected by alpha particle attenuation bias since it is based on the
483 relative increase of gross alpha activity. However, the waiting period to obtain the result is
484 longer since two gross alpha activity measurements are required, at 5 and 50 days, in order
485 to determine the initial $^{210}$Po/$^{210}$Pb ratio. What is more, this method is based on the
486 assumption that the relative increase of gross alpha activity is equal to the $^{210}$Po true relative
487 increase in the filter. Potential reasons for rejecting this assumption would be the presence
488 of other alpha emitters in the filter. Regarding long-lived radionuclides, the comparison at 50
489 days between gross alpha activity and $^{210}$Po activity demonstrates that no contribution can

be detected since an excellent correlation is found between the two activities. However, short-lived radionuclides with significant initial activity compared to $^{210}$Po could have completely decayed and could be missed at 50 days. Such radionuclides would likely have a half-life shorter than ~10 days. Conversely, they must have a half-life > ~1 day to be still active in the sample at 5 days (this is not the case for all radon and thoron daughters). A search in a radionuclide database indicates that potential candidates for naturally occurring alpha-emitters with a half-life between 1 and 10 days are $^{223}$Ra and $^{224}$Ra. For both nuclides, we found no atmospheric activity reported in the literature. However, airborne $^{228}$Th ($^{224}$Ra father in the $^{232}$Th decay chain) activity has occasionally been reported to be about 1 µBq/m$^3$ (Kolb, 1989). Therefore we suggest that $^{224}$Ra activity level is in the same order of magnitude due its short half-life (3.6 days). Such level is very low compared to the amplitude of gross alpha activity variation (tens of µBq/m$^3$) and would not affect the final result. Because $^{223}$Ra originates from the $^{235}$U decay chain, which is much less abundant than $^{232}$Th and $^{238}$U in nature (0.7% of uranium and Th/U = 4.2), we suggest that $^{223}$Ra levels in the atmosphere are likely to be even lower than $^{224}$Ra levels. Therefore, it appears that the initial assumption lying behind the method is robust.

When compared in term of final result uncertainty, the gross alpha activity variation method is more reliable than direct $^{210}$Po determination if the time lag between sampling and $^{210}$Po determination is long (typically 50-70 days). Conversely, if the time lag is short (10-20 days) the two methods give similar results, even if the typical relative uncertainty is higher for the gross alpha activity variation method as compared to direct $^{210}$Po determination (50% compared to 35%). Since both methods are based on measured $^{210}$Pb activity, it should finally be noted that the uncertainty of both methods would decrease if a more precise $^{210}$Pb activity measurement is available.

514 4.4 Alpha/beta activity ratio versus $^{210}Po/^{210}Pb$ activity ratio and the detection of

515 extreme natural events

516 5-day alpha and beta activities are routinely measured in many locations for

517 monitoring reasons. Thus, large databases of alpha/beta activity ratio are available and could

518 be used to study $^{210}Po$ and $^{210}Pb$ in the atmosphere. When comparing this ratio with our

519 estimates of $^{210}Po/^{210}Pb$ activity ratio, we found that both ratios match each other due to

520 large uncertainties. Due to the rather low number of samples (16) and to the fact that

521 $^{210}Po/^{210}Pb$ and gross alpha/beta ratio variability did not significantly exceed the

522 measurement uncertainty, it is not possible to conclude about the correlation between the

523 two ratios. However, when looking at mean ratios, our data suggest that alpha/beta activity

524 ratio is smaller than $^{210}Po/^{210}Pb$ activity ratio. This underestimation is potentially due to two

525 phenomena: (i) presence of other beta emitters leading to an overestimation of $^{210}Pb$ by

526 gross beta activity and (ii) calibration error on alpha measurement due to an inappropriate

527 treatment of alpha self-absorption in the filter, leading to underestimation of $^{210}Po$ by gross

528 alpha activity.

529 The amplitude of these two biases has been determined in sections 3.2, 3.4, 3.5 and 3.6.

530 Considering the mean and standard deviation of alpha/$^{210}Po$ ratios (see figures 5 and 6a, b)

531 determined at 5 and 50 days with different methods, it is possible to infer a typical

532 alpha/$^{210}Po$ ratio of 0.7 with a sample-to-sample variability of 15%. At 5 days, the beta/$^{210}Pb$

533 ratio has a mean value of 1.5 with a variability of 15%. Thus, it is possible to infer a typical

534 factor of 0.5 between gross alpha/beta and $^{210}Po/^{210}Pb$ activity ratios with a 1σ variability of

535 20%. Consequently, the gross alpha/beta activity ratio appears to be suitable for tracking

536 relative $^{210}Po/^{210}Pb$ ratio variations much larger than 20% (*i.e.* at least 100%). Yet, relative

variations of $^{210}$Po activity associated with savanna fire plumes or volcanic plumes often exceed this threshold as reported by several authors (e.g., Le Cloarec et al., 1995; Nho et al., 1996, 1997). Therefore, the gross alpha/beta ratio might be able to record such variations. Finally it is possible to imagine a protocol dedicated to the monitoring of these extreme natural events:

- The protocol is triggered on when 5-day alpha/beta ratio is 100% larger than the reference value.
- A gamma spectrometry is performed as long as possible to obtain $^{210}$Pb activity in the sample.
- If possible, an aliquot is analysed as soon as possible for $^{210}$Po determination.
- In any case, several gross alpha/beta countings are performed during 50 days to better constrain the initial $^{210}$Bi/$^{210}$Pb and $^{210}$Po/$^{210}$Pb ratios and the cosmogenic radionuclides.

## 5. Conclusion

Gross alpha/beta activity and specific $^{210}$Po and $^{210}$Pb activity measurements have been performed on a set of atmospheric aerosols samples in order to investigate co-variations of these different activities. Several main conclusions can be drawn:

- Beta activity was found to systematically overestimate $^{210}$Pb activity by ~30%. Using 5 and 50-day gross beta activity measurements, it is possible to constrain the nature of this beta activity excess. We show that it is mostly due to short-lived beta emitters ($^{33}$P, $^{32}$P, and $^{35}$S).

- 50-day gross alpha activity is mainly due to $^{210}$Po. However, alpha activity is found to underestimate $^{210}$Po activity. This is likely due to the alpha energy attenuation in the filter that is difficult to properly take into account in the calibration process.

- Determination of $^{210}$Po activity in the atmosphere from delayed $^{210}$Po measurement (from 15 to 90 days after sampling in this study) is very challenging due to the effect of $^{210}$Po build-up from $^{210}$Pb and $^{210}$Bi decay. We show that the uncertainty increases as the timespan of correction increases and that the corrected value can be significantly biased.

- However, indirect estimation of $^{210}$Po/$^{210}$Pb activity ratio can be obtained from gross alpha activity variation between 5 and 50 days. Mean $^{210}$Po/$^{210}$Pb activity ratio obtained using this method is in very good agreement with alpha/$^{210}$Pb activity ratio, meaning that the method is not strongly biased although it is indirect.

- alpha/beta activity ratio tend to underestimate $^{210}$Po/$^{210}$Pb activity ratios due to discrepancies between gross beta and $^{210}$Pb activities (presence of other beta emitters), on one hand, and between gross alpha and $^{210}$Po activities on the other hand (alpha particle attenuation). However, large-scale $^{210}$Po/$^{210}$Pb ratio variations typical of extreme natural events could still be monitored through gross alpha/beta measurements.

584 - A first estimation of atmospheric $^{210}Po$ activity level in France is 13 ± 6 µBq/m$^3$.

585

586

## APPENDIX A: correction of $^{210}$Po build-up in the filter.

$^{210}$Po activity measured at a given time *t* must be corrected to take into account the build-up of this radionuclide by $^{210}$Bi decay in the sample. The formula of this correction can be obtained by solving the decay equations for a three-member chain (1→2→3, or $^{210}$Pb→$^{210}$Bi→$^{210}$Po). To do so we use the formalism of Bateman given by Pressyanov (2002) where radionuclide initial numbers are factorized and we transform it to express the solution with activities instead of numbers:

$$A_i(t) = A_{i,0}e^{-\lambda_i t} + \sum_{m=1}^{i-1} A_{m,0} \prod_{q=m+1}^{i} \lambda_q \sum_{k=m}^{i} \frac{e^{-\lambda_k t}}{\prod_{j=m\,(j\neq k)}^{i}(\lambda_j - \lambda_k)}$$

(eq. A.1)

were $A_i(t)$ stands for the activity of the i-th nuclide in the decay chain, $A_{i,0}(t)$ for the initial activity of $i$ (at $t = 0$), $\lambda_i$ for the decay constant of $i$ and $t$ for the time. In the case of $^{210}$Pb -> $^{210}$Bi -> $^{210}$Po (1->2->3) decay chain, the equation A.1 translates to:

$$(\mathrm{Po})_t = (\mathrm{Po})_0 C_{\mathrm{Po}}^t + (\mathrm{Bi})_0 C_{\mathrm{Bi}}^t + (\mathrm{Pb})_0 C_{\mathrm{Pb}}^t$$

(eq. A.2)

where $(\mathrm{X})_0$ is the activity of the aliquot at a given initial time and $(\mathrm{X})_t$ is the activity of the same aliquot after a time *t* (X corresponding either with $^{210}$Pb, $^{210}$Bi or $^{210}$Po, the 210 exponent is not reproduced in the equation for simplicity). $C_{\mathrm{X}}^t$ is a numerical coefficient that is a function of time *t* and of radioactive decay constants of $^{210}$Pb, $^{210}$Bi and $^{210}$Po:

$$C_{\mathrm{Po}}^t = e^{-\lambda_{\mathrm{Po}} t}$$

$$C_{\mathrm{Bi}}^t = \frac{\lambda_{\mathrm{Po}}}{\lambda_{\mathrm{Po}} - \lambda_{\mathrm{Bi}}} e^{-\lambda_{\mathrm{Bi}} t} + \frac{\lambda_{\mathrm{Po}}}{\lambda_{\mathrm{Bi}} - \lambda_{\mathrm{Po}}} e^{-\lambda_{\mathrm{Po}} t}$$

$$C_{\mathrm{Pb}}^{t} = \frac{\lambda_{\mathrm{Po}}\lambda_{\mathrm{Bi}}}{(\lambda_{\mathrm{Po}} - \lambda_{\mathrm{Pb}})(\lambda_{\mathrm{Bi}} - \lambda_{\mathrm{Pb}})} e^{-\lambda_{\mathrm{Pb}}t} + \frac{\lambda_{\mathrm{Po}}\lambda_{\mathrm{Bi}}}{(\lambda_{\mathrm{Po}} - \lambda_{\mathrm{Bi}})(\lambda_{\mathrm{Pb}} - \lambda_{\mathrm{Bi}})} e^{-\lambda_{\mathrm{Bi}}t}$$

$$+ \frac{\lambda_{\mathrm{Po}}\lambda_{\mathrm{Bi}}}{(\lambda_{\mathrm{Bi}} - \lambda_{\mathrm{Po}})(\lambda_{\mathrm{Pb}} - \lambda_{\mathrm{Po}})} e^{-\lambda_{\mathrm{Po}}t}$$

(eqs. A.3, A.4 & A.5)

Using this formalism it is possible to infer initial polonium content of the sample using the following equation:

$$(\mathrm{Po})_0 = \frac{(\mathrm{Po})_t - (\mathrm{Bi})_0 C_{\mathrm{Bi}}^{t} - (\mathrm{Pb})_0 C_{\mathrm{Pb}}^{t}}{C_{\mathrm{Po}}^{t}}$$

(eq. A.6)

In the right member of equation A.6, $(\mathrm{Po})_t$ is measured, $(\mathrm{Pb})_0$ is constant through short times and is determined by gamma spectrometry and $C_{\mathrm{Bi}}^{t}$, $C_{\mathrm{Pb}}^{t}$ and $C_{\mathrm{Po}}^{t}$ are directly calculated from $t$. Only $(\mathrm{Bi})_0$ is not directly measured. When $^{210}$Po activity is to be recalculated at 50-day analysis time, $(\mathrm{Bi})_0$ is equal to $(\mathrm{Pb})_0$ because of radioactive equilibrium and equation A.6 simplifies. When $^{210}$Po activity is to be recalculated at sampling time, or at 5 days, it is not possible to assume radioactive equilibrium. However, it is possible to show that the initial $^{210}$Bi activity can be neglected. Let us rewrite equation A.6:

$$(\mathrm{Po})_0 = \frac{(\mathrm{Po})_t}{C_{\mathrm{Po}}^{t}} - \frac{(\mathrm{Pb})_0 C_{\mathrm{Pb}}^{t}}{C_{\mathrm{Po}}^{t}} \left(1 + \frac{(\mathrm{Bi})_0}{(\mathrm{Pb})_0} \frac{C_{\mathrm{Bi}}^{t}}{C_{\mathrm{Pb}}^{t}}\right)$$

(eq. A.7)

We can neglect the contribution of $^{210}$Bi initial activity if it is smaller than the $^{210}$Pb term contribution, in other words if:

$$\frac{(\mathrm{Bi})_0}{(\mathrm{Pb})_0} \frac{C_{\mathrm{Bi}}^{t}}{C_{\mathrm{Pb}}^{t}} \ll 1$$

618 (eq. A.8)

619 First, $C_{\mathrm{Bi}}^{t}/C_{\mathrm{Pb}}^{t}$ is about 10% for $t$ = 50 days. Second, $^{210}$Bi/$^{210}$Pb activity ratio of atmospheric
620 aerosols is generally reported lower than 1 with a mean value of 0.5 (e.g. Poet et al., 1972).
621 Therefore, it is likely that the contribution of the $^{210}$Bi term in equation 4 is no more than 10
622 % of the contribution of $^{210}$Pb, and likely around 5 %. Because the typical uncertainty on
623 $^{210}$Pb values measured by gamma spectrometry is larger than 10 % (see table 1), it is
624 legitimate to neglect $^{210}$Bi initial activity in the correction formula. Equation A.7 can thus be
625 simplified as:

$$(\mathrm{Po})_0 = \frac{(\mathrm{Po})_t - (\mathrm{Pb})_0 C_{\mathrm{Pb}}^{t}}{C_{\mathrm{Po}}^{t}}$$

626 (eq. A.9)

627 Finally, the uncertainty of corrected $^{210}$Po activity is obtained by convolution of the
628 uncertainties of $^{210}$Po and $^{210}$Pb measurements:

$$u((\mathrm{Po})_0) = \frac{1}{C_{\mathrm{Po}}^{t}} \sqrt{u^2((\mathrm{Po})_t) + u^2((\mathrm{Pb})_0) {C_{\mathrm{Pb}}^{t}}^2}$$

629 (eq. A.10)

630 where $u(v)$ stands for the uncertainty on the measured quantity $v$.

631

632

633

634

## Appendix B: determination of $^{210}$Po/$^{210}$Pb activity ratio from gross alpha activity increase between 5 and 50 days.

Supposing that gross alpha activity relative variation between 5 and 50 days is only due to $^{210}$Po, we can write:

$$\frac{\alpha_{50} - \alpha_5}{\alpha_5} = \frac{(\mathrm{Po})_{50} - (\mathrm{Po})_5}{(\mathrm{Po})_5}$$

(eq. B.1)

where $\alpha$ and $(\mathrm{Po})_t$ correspond to gross alpha activity and $^{210}$Po activity respectively (either at 5 or 50 days). Replacing right terms of equation B.1 by their expression given by equation A.2, the relative variation of gross alpha activity becomes:

$$\frac{\alpha_{50} - \alpha_5}{\alpha_5} = \frac{\left(C_{\mathrm{Pb}}^{50} - C_{\mathrm{Pb}}^{5}\right)(\mathrm{Pb})_0 + \left(C_{\mathrm{Bi}}^{50} - C_{\mathrm{Bi}}^{5}\right)(\mathrm{Bi})_0 + \left(C_{\mathrm{Po}}^{50} - C_{\mathrm{Po}}^{5}\right)(\mathrm{Po})_0}{C_{\mathrm{Pb}}^{5}(\mathrm{Pb})_0 + C_{\mathrm{Bi}}^{5}(\mathrm{Bi})_0 + C_{\mathrm{Po}}^{5}(\mathrm{Po})_0}$$

$$= \frac{\Delta C_{\mathrm{Pb}}(\mathrm{Pb})_0 + \Delta C_{\mathrm{Bi}}(\mathrm{Bi})_0 + \Delta C_{\mathrm{Po}}(\mathrm{Po})_0}{C_{\mathrm{Pb}}^{5}(\mathrm{Pb})_0 + C_{\mathrm{Bi}}^{5}(\mathrm{Bi})_0 + C_{\mathrm{Po}}^{5}(\mathrm{Po})_0}$$

(eq. B.2)

where $\Delta C_{\mathrm{X}} = C_{\mathrm{X}}^{50} - C_{\mathrm{X}}^{5}$. Dividing by $(\mathrm{Po})_0$ and using the notation $R_0$ for $^{210}$Po/$^{210}$Pb initial activity ratio, equation B.2 becomes:

$$\frac{\alpha_{50} - \alpha_5}{\alpha_5} = \frac{\Delta C_{\mathrm{Pb}} R_0^{-1} + \Delta C_{\mathrm{Bi}}(\mathrm{Bi/Pb})_0 R_0^{-1} + \Delta C_{\mathrm{Po}}}{C_{\mathrm{Pb}}^{5} R_0^{-1} + C_{\mathrm{Bi}}^{5}(\mathrm{Bi/Pb})_0 R_0^{-1} + C_{\mathrm{Po}}^{5}}$$

(eq. B.3)

Noting $\delta = \frac{\alpha_{50} - \alpha_5}{\alpha_5}$ the relative variation of gross alpha activity, we can finally obtain an expression of $R_0$ as a function of $\delta$:

$$R_0 = \frac{C^5_{\mathrm{Pb}}\delta - \Delta C_{\mathrm{Pb}} + \left(\frac{\mathrm{Bi}}{\mathrm{Pb}}\right)_0 \left(C^5_{\mathrm{Bi}}\delta - \Delta C_{\mathrm{Bi}}\right)}{\Delta C_{\mathrm{Po}} - C^5_{\mathrm{Po}}\delta}$$

649 (eq. B.4).

650 Of course, this expression of $^{210}$Po/$^{210}$Pb activity ratio depends also on the $^{210}$Bi/$^{210}$Pb activity

651 ratio and can be simplified if an assumption on the $^{210}$Bi/$^{210}$Po initial activity ratio is made.

652

653

## References


Allard, P., Aiuppa, A., Bani, P., Métrich, N., Bertagnini, A., Gauthier, P.-J., Shinohara, H., Sawyer, G., Parello, F., Bagnato, E., Pelletier, B., Garaebiti, E., 2016. Prodigious emission rates and magma degassing budget of major, trace and radioactive volatile species from Ambrym basaltic volcano, Vanuatu island Arc. Journal of Volcanology and Geothermal Research, Understanding volcanoes in the Vanuatu arc 322, 119–143. https://doi.org/10.1016/j.jvolgeores.2015.10.004

Baskaran, M., 2016. Applications of Radon Progeny in Atmospheric Studies, in: Baskaran, M. (Ed.), Radon: A Tracer for Geological, Geophysical and Geochemical Studies, Springer Geochemistry. Springer International Publishing, Cham, pp. 85–117. https://doi.org/10.1007/978-3-319-21329-3_5

Baskaran, M., 2011. Po-210 and Pb-210 as atmospheric tracers and global atmospheric Pb-210 fallout: a Review. Journal of Environmental Radioactivity, International Topical Meeting on Polonium and Radioactive Lead Isotopes 102, 500–513. https://doi.org/10.1016/j.jenvrad.2010.10.007

Bourcier, L., Masson, O., Laj, P., Pichon, J.M., Paulat, P., Freney, E., Sellegri, K., 2011. Comparative trends and seasonal variation of 7Be, 210Pb and 137Cs at two altitude sites in the central part of France. Journal of Environmental Radioactivity 102, 294–301. https://doi.org/10.1016/j.jenvrad.2010.12.005

Daish, S.R., Dale, A.A., Dale, C.J., May, R., Rowe, J.E., 2005. The temporal variations of 7Be, 210Pb and 210Po in air in England. Journal of Environmental Radioactivity 84, 457–467. https://doi.org/10.1016/j.jenvrad.2005.05.003

Garland, J.A., Wakeford, R., 2007. Atmospheric emissions from the Windscale accident of October 1957. Atmospheric Environment 41, 3904–3920. https://doi.org/10.1016/j.atmosenv.2006.12.049

Geryes, T., Monsanglant-Louvet, C., Gehin, E., 2009. Experimental and simulation methods to evaluate the alpha self-absorption factors for radioactive aerosol fiber filters. Radiation Measurements, Proceedings of the 24th International Conferenceon Nuclear Tracks in Solids 44, 763–765. https://doi.org/10.1016/j.radmeas.2009.10.059

Hernández, F., Hernández-Armas, J., Catalán, A., Fernández-Aldecoa, J.C., Karlsson, L., 2005. Gross alpha, gross beta activities and gamma emitting radionuclides composition of airborne particulate samples in an oceanic island. Atmospheric Environment 39, 4057–4066. https://doi.org/10.1016/j.atmosenv.2005.03.035

Kolb, W., 1989. Seasonal fluctutions of the uranium and thorium contents of aerosols in ground-level air. Journal of Environmental Radioactivity 9, 61–75. https://doi.org/10.1016/0265-931X(89)90038-6

Lal, D., Suess, H.E., 1968. The Radioactivity of the Atmosphere and Hydrosphere. Annual Review of Nuclear Science 18, 407–434. https://doi.org/10.1146/annurev.ns.18.120168.002203

Le Cloarec, M.F., Ardouin, B., Cachier, H., Liousse, C., Neveu, S., Nho, E.-Y., 1995. 210Po in savanna burning plumes. J Atmos Chem 22, 111–122. https://doi.org/10.1007/BF00708184

Lozano, R.L., Miguel, E.G.S., Bolívar, J.P., 2011. Assessment of the influence of in situ 210Bi in the calculation of in situ 210Po in air aerosols: Implications on residence time calculations using 210Po/210Pb activity ratios. Journal of Geophysical Research: Atmospheres 116. https://doi.org/10.1029/2010JD014915

Lujanien≒, G., Ogorodnikov, B.I., Budyka, A.K., Skitovich, V.I., Lujanas, V., 1997. An investigation of changes in radionuclide carrier properties. Journal of Environmental Radioactivity 35, 71–90. https://doi.org/10.1016/S0265-931X(96)00014-8

Mattsson, R., Paatero, J., Hatakka, J., 1996. Automatic Alpha/Beta Analyser for Air Filter Samples - Absolute Determination of Radon Progeny by Pseudo-Coincidence Techniques. Radiat Prot Dosimetry 63, 133–139. https://doi.org/10.1093/oxfordjournals.rpd.a031520

Moore, M.E., McFarland, A.R., Rodgers, J.C., 1993. Factors That Affect Alpha Particle Detection in Continuous Air Monitor Applications. Health Physics 65, 69–81.

Nho, E.-Y., Ardouin, B., Le Cloarec, M.F., Ramonet, M., 1996. Origins of 210Po in the atmosphere at lamto, ivory coast: Biomass burning and saharan dusts. Atmospheric Environment 30, 3705–3714. https://doi.org/10.1016/1352-2310(96)00093-3

Nho, E.-Y., Cloarec, M.-F.L., Ardouin, B., Ramonet, M., 1997. 210Po, an atmospheric tracer of long-range transport of volcanic plumes. Tellus B: Chemical and Physical Meteorology 49, 429–438. https://doi.org/10.3402/tellusb.v49i4.15980

OPERA network [WWW Document], n.d. URL https://www.irsn.fr/en/research/scientific-tools/experimental-facilities-means/opera/Pages/Opera-network.aspx (accessed 6.17.20).

Paatero, J., Vesterbacka, K., Makkonen, U., Kyllönen, K., Hellen, H., Hatakka, J., Anttila, P., 2009. Resuspension of radionuclides into the atmosphere due to forest fires. Journal of Radioanalytical and Nuclear Chemistry 282, 473–476. https://doi.org/10.1007/s10967-009-0254-9

Poet, S.E., Moore, H.E., Martell, E.A., 1972. Lead 210, bismuth 210, and polonium 210 in the atmosphere: Accurate ratio measurement and application to aerosol residence time determination. Journal of Geophysical Research (1896-1977) 77, 6515–6527. https://doi.org/10.1029/JC077i033p06515

RNM [WWW Document], n.d. URL https://www.mesure-radioactivite.fr/en#/expert (accessed 6.17.20).

Schery, S.D., 2001. Understanding radioactive aerosols and their measurement. Springer Science & Business Media.

Sources and effects of ionizing radiation, UNSCEAR 2008 Report, 2010. . Volume I. Annex A. United Nations, New York.

## Figures and tables

**Table 1:** Sampling details and analysis results. All uncertainties are given with a coverage factor k=2. $^{210}$Po activity is given at the time of $^{210}$Po deposition onto plates. All activities are expressed in mBq/m$^3$ considering sampled volumes and a constant aliquot/filter surface ratio of 0.3.

| Sample | Sampling start (local time) | Sampling duration (h) | Sampled volume (m³) | Dust load (µg/m³) | 1st gross alpha/beta counting delay (d) | Gross activity 5 days (mBq/m3) | | 2nd gross alpha/beta counting delay (d) | Gross activity 50 days (mBq/m³) | | $^{210}$Pb activity (mBq/m3) | $^{210}$Po meas. delay (d) | $^{210}$Po activity (mBq/m³) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | alpha | beta | | alpha | beta | | | |
| 1 | 27/3/17 14:08 | 50,6 | 7582 | 3 | 7 | 0,011 ± 0,003 | 0,224 ± 0,009 | 63 | 0,038 ± 0,004 | 0,203 ± 0,009 | 0,18 ± 0,05 | 91 | 0,09 ± 0,01 |
| 2 | 4/4/17 11:33 | 73,8 | 11073 | 15 | 5 | 0,008 ± 0,002 | 0,203 ± 0,007 | 63 | 0,032 ± 0,003 | 0,178 ± 0,007 | 0,16 ± 0,04 | 82 | 0,055 ± 0,006 |
| 3 | 12/4/17 18:40 | 47,9 | 7181 | 15 | 11 | 0,017 ± 0,003 | 0,33 ± 0,01 | 56 | 0,055 ± 0,007 | 0,31 ± 0,02 | 0,21 ± 0,03 | 110 | 0,11 ± 0,01 |
| 4 | 14/4/17 18:35 | 87,0 | 13050 | 10 | 7 | 0,010 ± 0,002 | 0,257 ± 0,008 | 52 | 0,038 ± 0,003 | 0,224 ± 0,007 | 0,16 ± 0,02 | 71 | 0,067 ± 0,007 |
| 5 | 21/4/17 13:53 | 71,6 | 10742 | 10 | 10 | 0,020 ± 0,003 | 0,48 ± 0,01 | 56 | 0,069 ± 0,004 | 0,39 ± 0,01 | 0,30 ± 0,03 | 65 | 0,10 ± 0,01 |
| 6 | 2/5/17 12:54 | 45,9 | 6893 | 6 | 5 | 0,004 ± 0,003 | 0,180 ± 0,008 | 53 | 0,018 ± 0,003 | 0,138 ± 0,008 | 0,09 ± 0,02 | 82 | 0,045 ± 0,005 |
| 7 | 12/5/17 18:02 | 63,3 | 9485 | 5 | 4 | 0,007 ± 0,002 | 0,162 ± 0,007 | 56 | 0,025 ± 0,003 | 0,160 ± 0,007 | 0,10 ± 0,02 | 71 | 0,038 ± 0,005 |
| 8 | 23/5/17 13:45 | 51,9 | 7781 | 12 | 6 | 0,013 ± 0,003 | 0,39 ± 0,01 | 56 | 0,069 ± 0,005 | 0,39 ± 0,01 | 0,27 ± 0,03 | 69 | 0,10 ± 0,01 |
| 9 | 7/6/17 13:22 | 52,3 | 7843 | 12 | 7 | 0,008 ± 0,003 | 0,30± 0,01 | 56 | 0,035 ± 0,003 | 0,228 ± 0,009 | 0,19 ± 0,03 | 61 | 0,047 ± 0,005 |
| 10 | 13/6/17 11:49 | 52,3 | 7845 | 15 | 11 | 0,033 ± 0,003 | 0,77 ± 0,02 | 64 | 0,147 ± 0,007 | 0,75 ± 0,02 | 0,60 ± 0,05 | 69 | 0,19 ± 0,02 |
| 11 | 21/6/17 13:36 | 48,2 | 7228 | 23 | 6 | 0,035 ± 0,004 | 0,91 ± 0,02 | 112 | 0,30 ± 0,01 | 1,05 ± 0,03 | 0,68 ± 0,06 | 118 | 0,35 ± 0,04 |
| 12 | 26/2/18 15:45 | 49,1 | 7363 | 17 | 9 | 0,020 ± 0,003 | 0,47 ± 0,02 | | | | 0,28 ± 0,08 | 15 | 0,034 ± 0,005 |
| 13 | 18/4/18 9:08 | 52,1 | 7825 | 23 | 7 | 0,020 ± 0,003 | 0,66 ± 0,02 | | | | 0,45 ± 0,06 | 17 | 0,046 ± 0,007 |
| 14 | 20/6/18 9:05 | 49,9 | 7491 | 18 | 14 | 0,022 ± 0,004 | 0,45 ± 0,01 | | | | 0,29 ± 0,03 | 20 | 0,036 ± 0,005 |
| 15 | 27/6/18 9:45 | 47,7 | 7138 | 17 | 17 | 0,020 ± 0,003 | 0,37 ± 0,01 | | | | 0,22 ± 0,04 | 21 | 0,030 ± 0,003 |
| 16 | 21/9/18 16:14 | 64,3 | 9631 | 6 | 19 | 0,015 ± 0,002 | 0,248 ± 0,008 | | | | 0,12 ± 0,03 | 24 | 0,021 ± 0,002 |

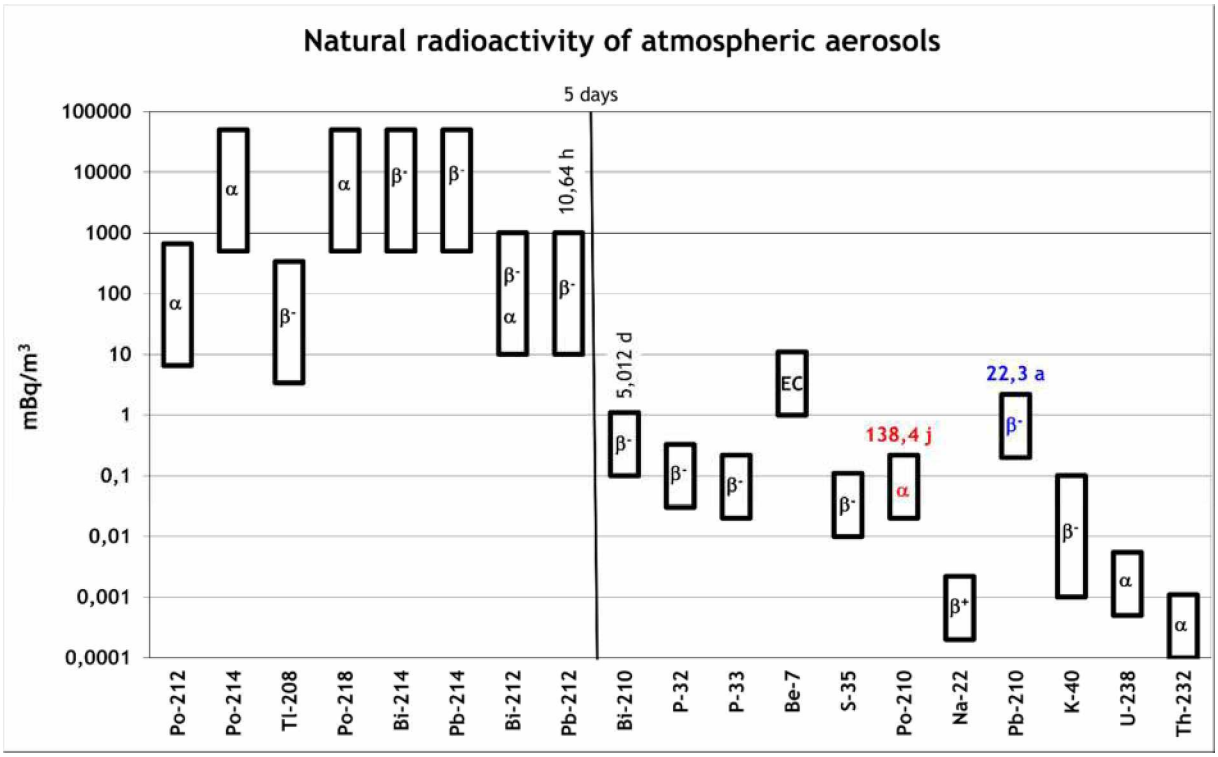


**Figure 1:** Repartition of the natural radioactivity of atmospheric aerosols. The main radionuclides are sorted on the x axis from short-period to long-period. The main decay mode (alpha, beta or electronic capture) is also indicated. Data are taken from the 2008 UNSCEAR report (Sources and effects of ionizing radiation, UNSCEAR 2008 Report, 2008) and from Schery (2001). All short-lived $^{222}$Rn daughters have half-lives considerably smaller than 5 days. Contrastingly, most $^{220}$Rn daughters (from the $^{232}$Th chain) are part of the progeny of $^{212}$Pb which has a 10.64 hours half-life. Therefore, the long-lived radioactivity can only be measured after 5 days when $^{212}$Pb has thoroughly decayed out (5 days corresponds with eleven $^{212}$Pb periods and a 2000 fold reduction of the initial activity). This long-lived radioactivity comes from three different types of radionuclides: long-lived $^{222}$Rn daughters ($^{210}$Pb, $^{210}$Bi, $^{210}$Po), radionuclides of cosmogenic origin ($^{32}$P, $^{33}$P, $^{7}$Be, $^{35}$S, $^{22}$Na) and "primordial" radionuclides ($^{40}$K, $^{238}$U, $^{232}$Th) injected in the atmosphere upon soil erosion. Long-lived alpha activity is largely dominated by $^{210}$Po. $^{210}$Pb is the most active long-lived beta emitter but other radionuclides are also significant ($^{32}$P, $^{33}$P, $^{35}$S, $^{40}$K).

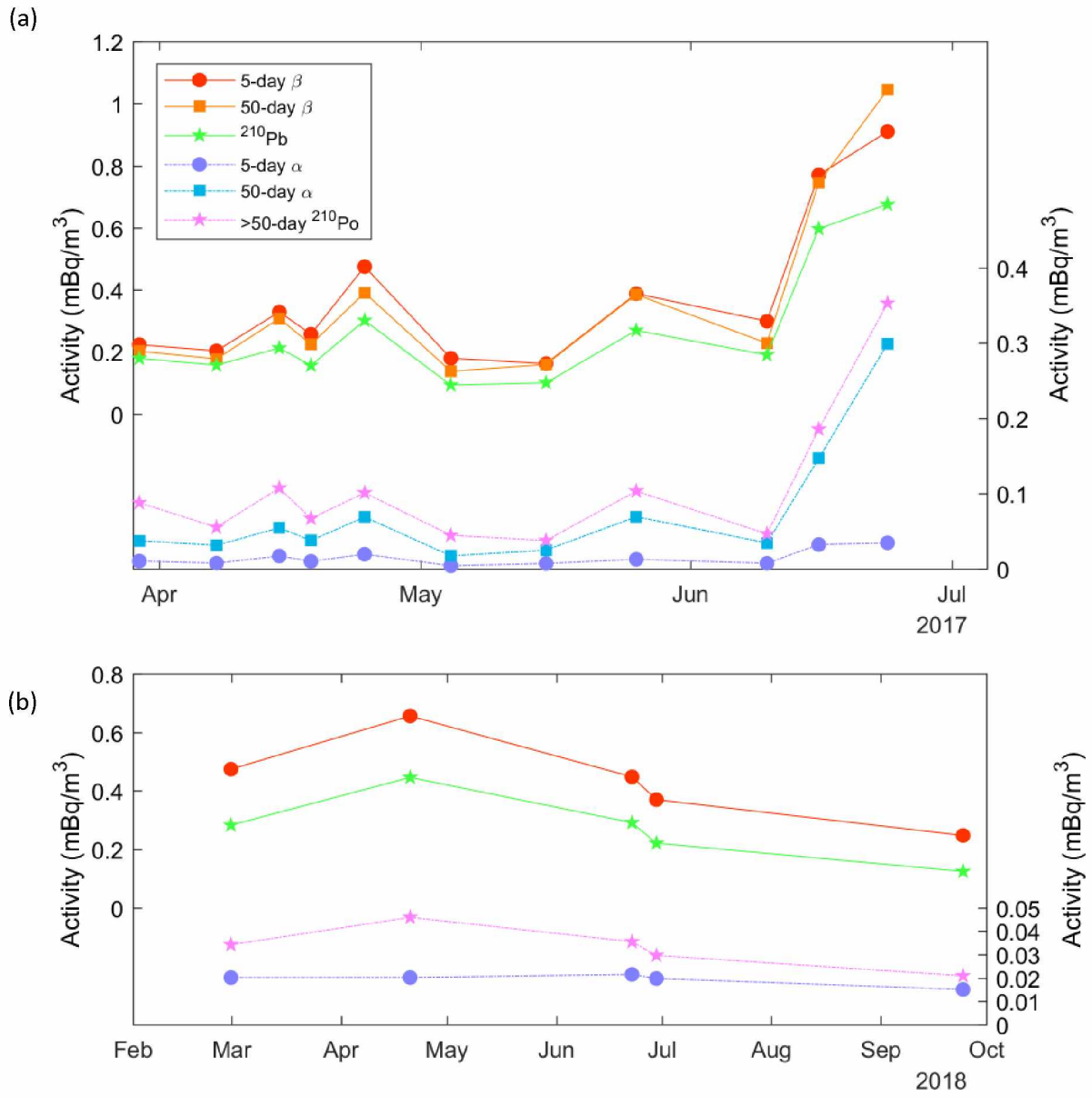


**Figure 2:** Activities recorded for all samples in 2017 (a) and 2018 (b), including 5 and 50-day gross alpha/beta activities, $^{210}$Pb activity measured by gamma spectrometry and $^{210}$Po activity measured by alpha spectrometry after chemical separation (activities reported on the graph are not corrected for $^{210}$Po ingrowth between sampling and measurement). Error bars are not drawn to avoid visual overload but are provided in table 1.

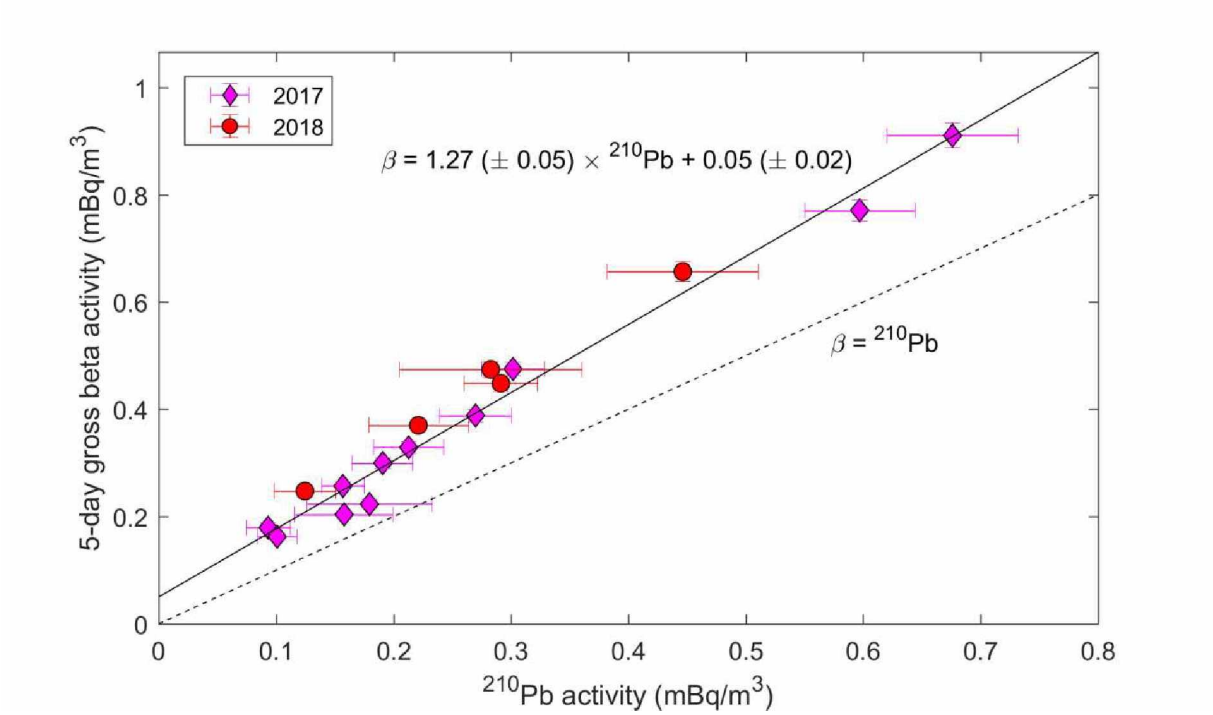


**Figure 3:** 5-day gross beta activity versus $^{210}$Pb activity of all samples (2017 and 2018 sample groups). The best linear fit ($R^2$ = 0.98) and the y=x line (dash line) are also plotted.

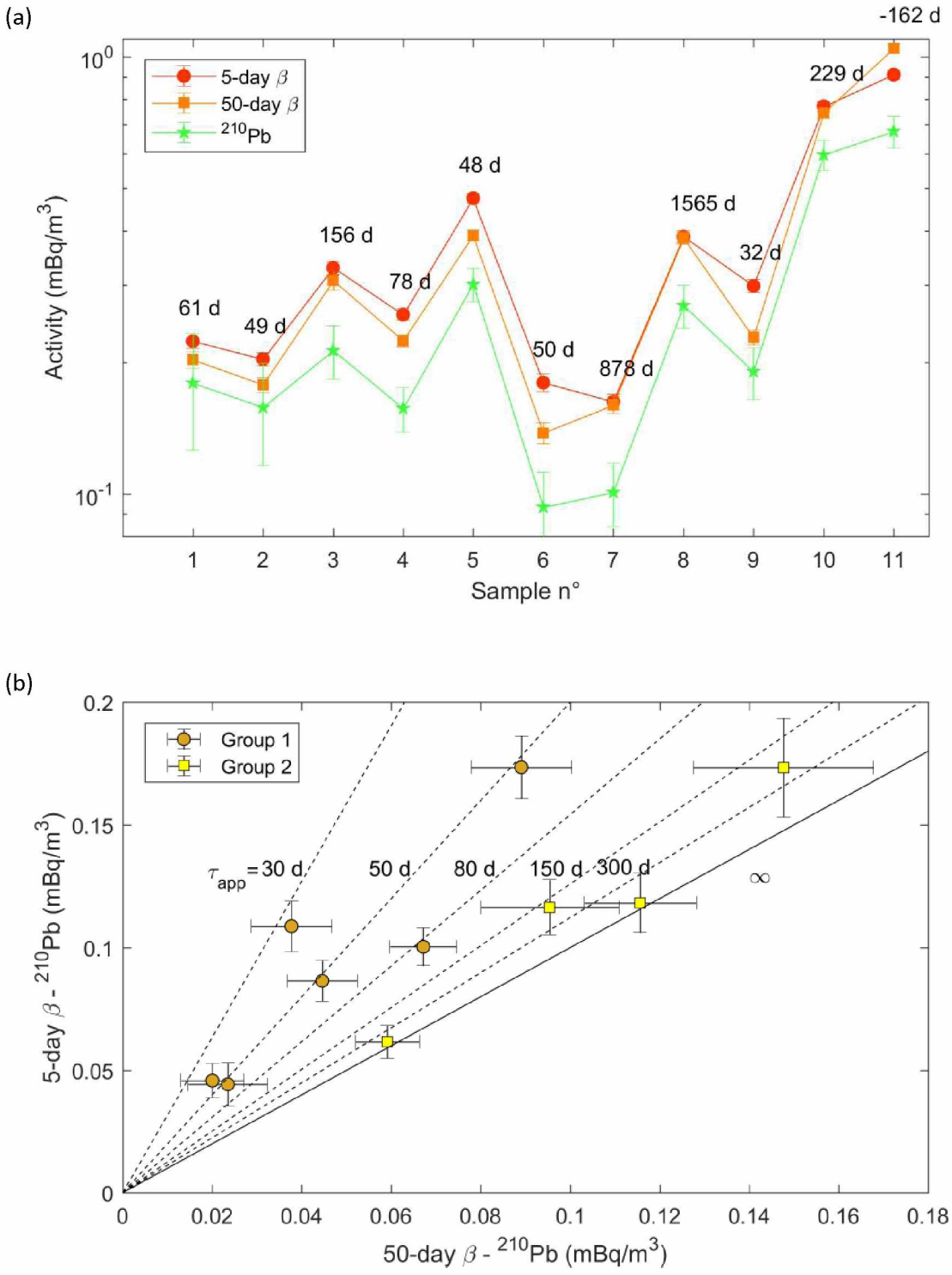


**Figure 4:** (a) 5-day and 50-day gross beta activities and $^{210}$Pb activity for all 2017 samples with the corresponding computed half-life of un-sustained beta activity decay (see section 3.3 for details) in days.

(b) Excess of gross beta activity relative to $^{210}Pb$ activity at 5 days (y axis) and at 50 days (x axis). Error bars are calculated taking into account gross beta activity uncertainty only. Iso-ligns of apparent half-life are also plotted for some values of the half-life (see section 3.3). Two groups are distinguished: group 1 for samples presenting significantly different 5 and 50-day gross beta activities at, group 2 for samples presenting similar 5 and 50-day gross beta activities.

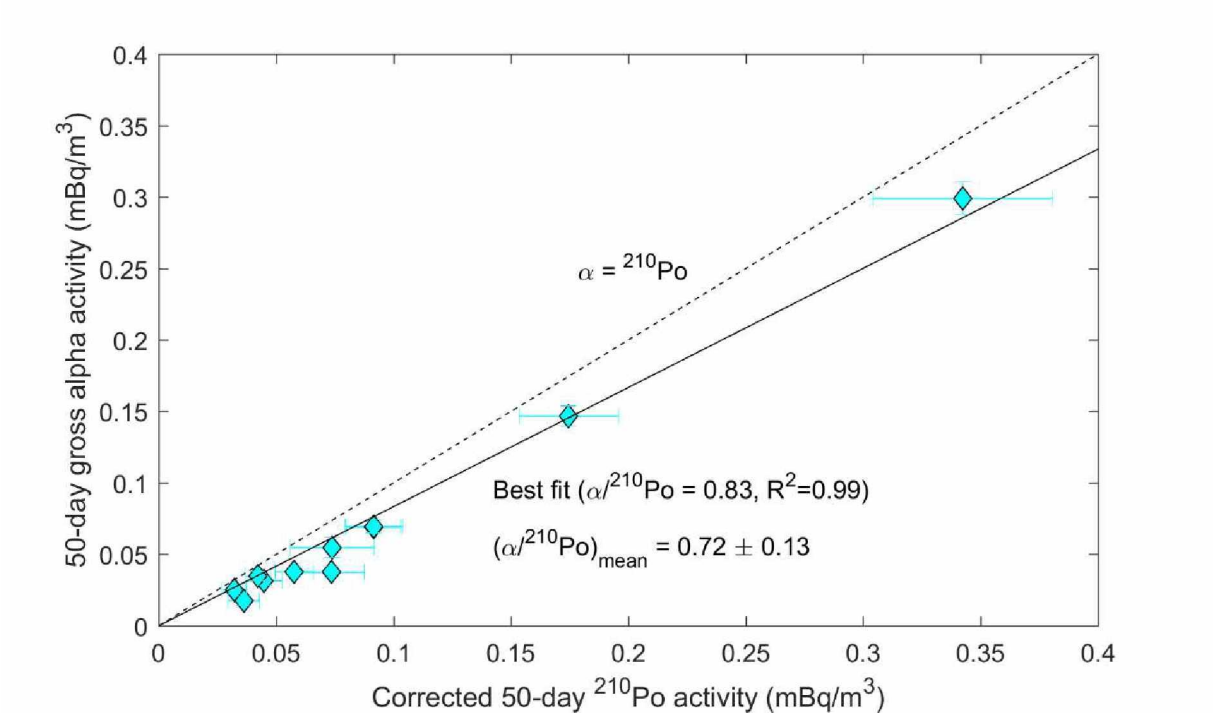


**Figure 5:** 50-day gross alpha activity versus $^{210}$Po activity recalculated at 50 days (2017 sample group, see appendix A for calculation details). The best linear fit ($R^2$ = 0.99) and the y=x line (dash line) are also plotted.

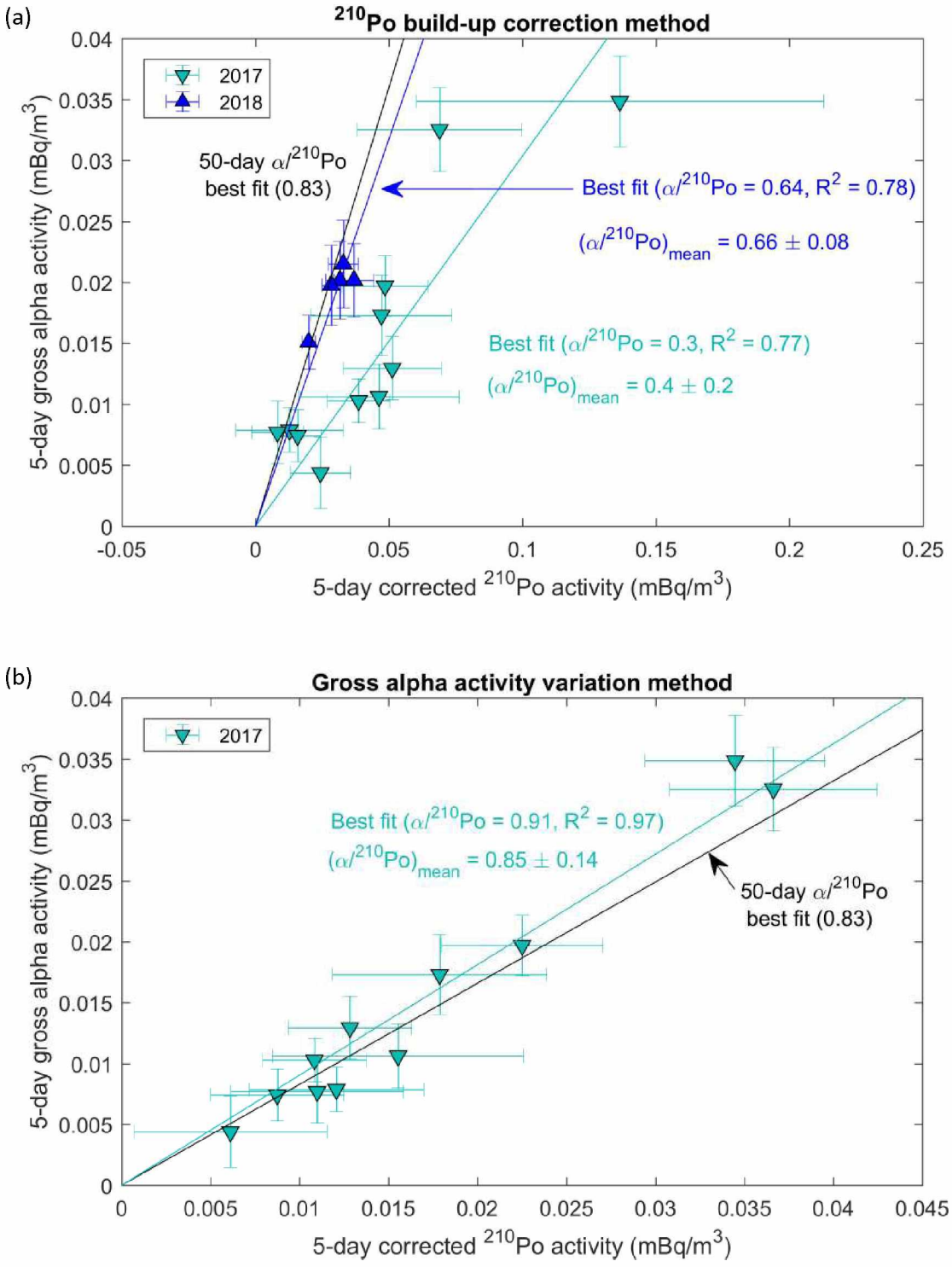


**Figure 6:** Correlation of 5-day gross alpha activity and $^{210}$Po activity recalculated at t = 5 days using different approaches: (a) build-up correction of $^{210}$Po activity (see appendix A for calculation details) and (b) determination of $^{210}$Po/$^{210}$Pb activity ratio from gross alpha activity variation between 5 and 50 days (see appendix B for calculation details). For each

method, the mean alpha/$^{210}$Po activity ratio is plotted (coloured lines) and compared to the alpha/$^{210}$Po measured at 50 days (0.83, black line). All uncertainties are propagated to the corrected $^{210}$Po activity. Moreover, mean and standard deviation of alpha/$^{210}$Po activity ratio are indicated in order to provide an estimation of the dispersion of obtained ratios, as well as $R^2$ coefficients.

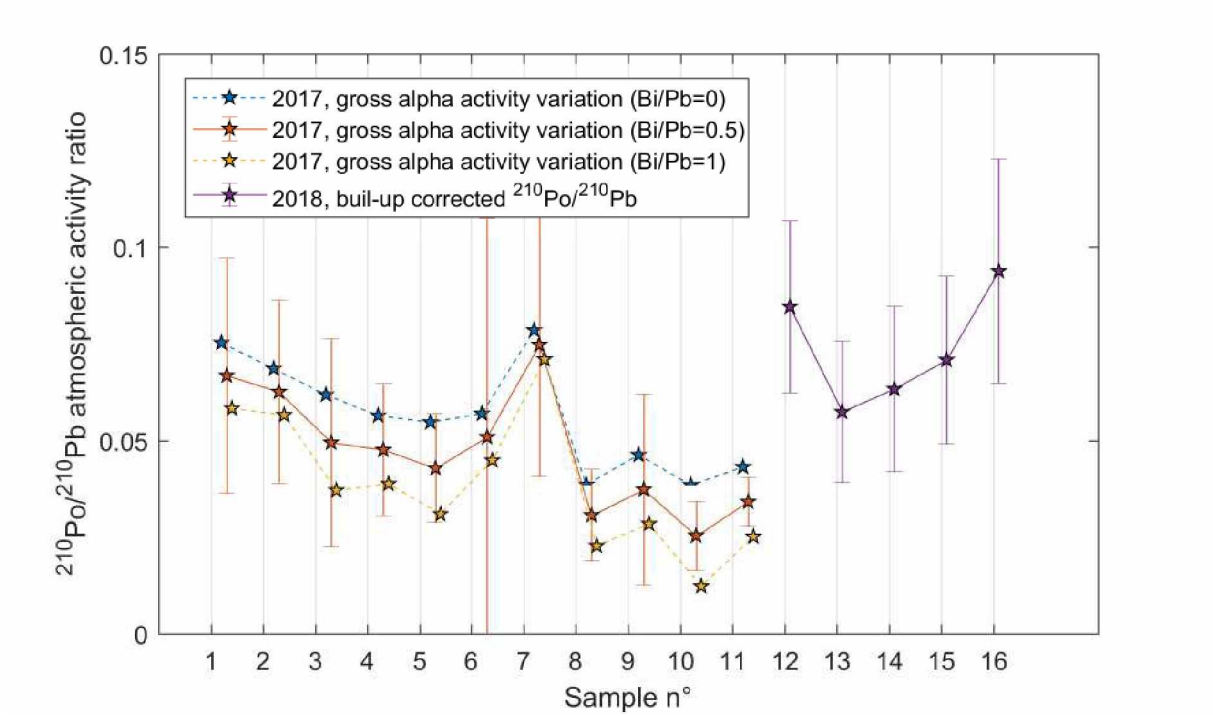


**Figure 7:** Comparison of atmospheric $^{210}$Po/$^{210}$Pb activity ratios at sampling time retrieved using gross alpha activity variation between 5 and 50 days (2017 samples, samples n°1 to 11) and build-up corrected $^{210}$Po activities divided by $^{210}$Pb activities (2018 sample group, samples n°12 to 16). Ratios inferred from gross alpha activity variation (blue, red and yellow lines) are represented for different assumed values of the $^{210}$Bi/$^{210}$Pb activity ratio (0, 0.5 and 1, respectively) and error bars (k=2) are propagated from uncertainties on 5 and 50-day gross alpha activities (error bars are only drawn on the red line). $^{210}$Po/$^{210}$Pb activity ratio determined from corrected $^{210}$Po activity and $^{210}$Pb activity are plotted with error bars corresponding to the uncertainty (k=2) on $^{210}$Po corrected activity value.

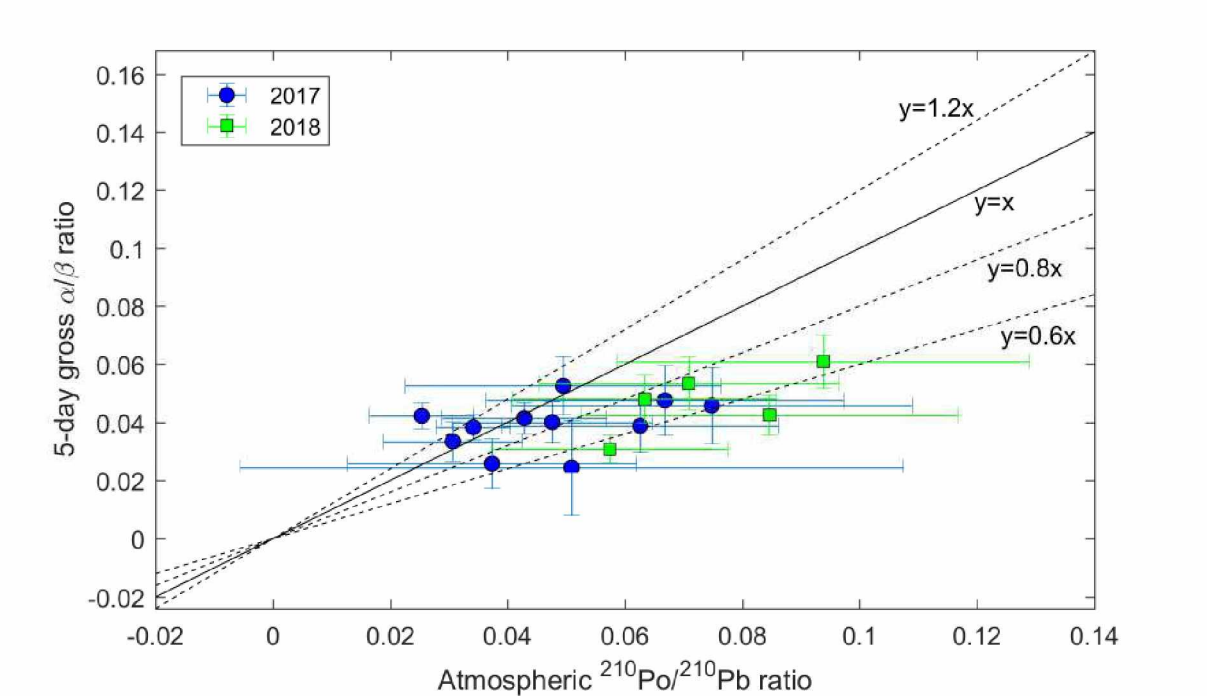


**Figure 8:** Gross alpha/beta activity ratio versus $^{210}Po/^{210}Pb$ activity ratios for 2017 samples (blue) and 2018 samples (green). For 2017 samples, $^{210}Po/^{210}Pb$ activity ratio is calculated using gross alpha activity variation between 5 and 50 days (see methods). For 2018 samples, $^{210}Po/^{210}Pb$ activity ratio is calculated using $^{210}Po$ and $^{210}Pb$ measurements with correction for $^{210}Po$ (see methods). All uncertainties have been propagated.