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- 2 What can gross alpha/beta activities tell about 210Po and 210Pb in
- 3 the atmosphere?
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10 What can gross alpha/beta activities tell about ²¹⁰Po and ²¹⁰Pb in the atmosphere?

Abstract: ²¹⁰Po and ²¹⁰Pb represent the most abundant part of atmospheric aerosol long-11 lived natural radioactivity. Moreover, ²¹⁰Pb-²¹⁰Po monitoring in the atmosphere can be of 12 interest for tracking extreme natural events that can enhance the level of alpha/beta 13 radioactivity in air. In this paper, we question the possibility to use routine gross alpha/beta 14 measurements in order to monitor 210 Po, 210 Pb and 210 Po/ 210 Pb ratio in the atmosphere. 15 Based on joint gross alpha/beta measurement and ²¹⁰Pb-²¹⁰Po specific determination on 16 16 atmosphere samples, we show that (i) gross beta activity systematically overestimates ²¹⁰Pb 17 activity due to the presence of interfering beta emitters and (ii) gross alpha activity mostly 18 reflects ²¹⁰Po activity even if an underestimation is always observed due to alpha particle 19 attenuation. In order to determine 210 Po/ 210 Pb ratio, we discuss the advantages of using 20 gross alpha activity time variation compared to specific ²¹⁰Po measurements. Finally, the 21 gross alpha/beta ratio appear to be a good proxy of the 210 Po/ 210 Pb ratio when large-scale 22 variations are to be monitored. We report a first reference level for the activity level of 23 airborne ²¹⁰Po in France of $13 \pm 6 \mu Bq/m^3$. 24 25

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32 **1. Introduction**

Long-lived radon daughters (namely ²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po) are widely used in 33 atmospheric studies (see recent reviews by Baskaran, 2011, 2016). These radionuclides can 34 be considered as tracers, as well as chronometers of air mass circulation. They are also 35 useful to determine the residence time and the removal rate of aerosols in the atmosphere. 36 In addition, they play a major role in the monitoring of atmospheric radioactivity because 37 38 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 39 40 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 41 atmospheric radioactivity monitoring and early warning context. 42 Extreme natural events such as volcanic eruptions, forest fires or dust resuspension events 43 are known to release important quantities of radioactive 210 Po into the atmosphere (*e.g.* 44 45 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 ²¹⁰Po into 46 the atmosphere at a rate of 210 TBq/year. In comparison, the estimated amount of 47 polonium released during the October, 1957 Windscale accident is 42 TBq (Garland and 48 Wakeford, 2007), which is to say only a fifth of the Ambrym cumulative emission in one year. 49 50 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 51 biomass or deserts), thus potentially increasing the exposure of local population to ionizing 52 radiations (²¹⁰Po is highly toxic when inhaled or ingested due to its very high specific activity 53

and emission of energetic alpha particles inside the body) and triggering anomalies of longlived alpha radioactivity in the atmosphere.

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

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

77 samples. For these two reasons, this technique is widely used in the field of aerosol radioactivity monitoring. As far as France is concerned, there is a very dense network of 78 nuclear power plants and other nuclear installations in France monitoring gross alpha/beta 79 air indices on a daily basis (this network is referred to as Réseau National de Mesures de la 80 radioactivité de l'environnement, see the RNM website in the references). Therefore, if 81 alpha/beta gross activity ratio is found to be well representative of the 210 Po/ 210 Pb ratio it 82 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.

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

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

104

105 **2. Methods**

106 2.1 <u>Atmospheric sampling</u>

107 Atmospheric aerosols have been sampled on the top of the building of the 108 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 109 elevation of about 400 m. We used a MegaVol-3000 particulate air sampler from Ecotech 110 111 that was operated at a flow rate of 150 m^3/h . Air was pumped through a polypropylene filter 112 (3M) similar to the filters of OPERA-AIR network (see OPERA network website in the 113 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 23 114 cm (414 cm²). 115

116 Eleven samples were collected on a weekly basis between March and June 2017. Five more

117 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

119 8,400 m³. Starting time and sampling duration were decided in order to avoid important

120 precipitation events and shifts of meteorological regimes during sampling.

121 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.

123

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 ²¹⁰Pb measurement by 129 _ 130 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 131 radon and thoron daughters (see figure 1). These analyses will be referred to as 132 the 5-day analyses hereafter for convenience, even if some of them were not 133 exactly performed 5 days after sampling (see table 1). 5-day gross alpha/beta 134 135 counting is a typical measurement for most of atmospheric radioactivity monitoring systems and such measurements are commonly available in many 136 places in France through a common sharing platform (see RNM website in the 137 references). 138

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 ²¹⁰Bi and ²¹⁰Pb (²¹⁰Bi is the daughter of ²¹⁰Pb and has a halflife 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

146	analyses. Indeed, this second set of measurements allows to make a direct
147	comparison between 210 Pb and gross beta activity. Actually, 210 Pb can only be
148	indirectly measured by the alpha/beta counter through the decay of its daughter
149	^{210}Bi because the beta end-point energies of ^{210}Pb are too low (i.e. $\text{E}_{\text{max}}\text{=}17$ and 63
150	keV) to produce detectable electrons, while 210 Bi has a much higher beta end-
151	point energy (E_{max} = 1162 keV). After 50 days, ²¹⁰ Bi activity is equal to ²¹⁰ Pb
152	activity and then any difference between gross beta activity and 210 Pb activity is
153	necessarily due to other radionuclides present in the filter.
154 -	Step 3: specific measurement of ²¹⁰ Po by alpha spectrometry after mineralization
155	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 ²¹⁰Po build-up in the sample before the measurement by alpha spectrometry.

161

2.3 Meaning of gross alpha/beta activities

Detection yields of gross alpha/beta counting detectors have been determined using ⁹⁰Sr-⁹⁰Y sources for beta and ²³⁹Pu 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 ⁹⁰Sr activity and gross alpha activity is expressed as equivalent ²³⁹Pu activity.

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

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

192 2.4 <u>Correction of ²¹⁰Po build-up in the filter</u>

Since ²¹⁰Pb has a 22.2 years half-life, it can be considered as stable during the whole 193 sampling and analysis periods. This is not the case for ²¹⁰Po due to its much shorter half-life 194 of only 138.4 days. Because the time lag between sampling and ²¹⁰Po analysis (typically 50-195 70 days) is not negligible compared to 210 Po half-life, and because of the presence of 210 Pb 196 and ²¹⁰Bi in the filter, ²¹⁰Po can be regenerated (or eventually decay in the case of initial 197 210 Po/ 210 Pb activity ratio greater than 1) in between the sampling time and the 198 measurement time. Thus, a correction has to be applied in order to infer the activity of the 199 filter at a given initial time prior to ²¹⁰Po measurement (either sampling time, 5-day or 50-200 day analyses times). Since ²¹⁰Po can be regenerated in the filter by the decay of his parent 201 210 Bi, itself sustained by the decay of 210 Pb, the correction depends on 210 Pb, 210 Bi and 210 Po 202 203 initial activities. The correction formula is given in appendix A. If necessary, the unknown ²¹⁰Bi activity can be neglected (see appendix A). 204

205 2.5 Volume normalisation.

Atmospheric activities are finally calculated from the activities measured on the aliquot (and subsequently corrected for ²¹⁰Po 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.

210

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 ²¹⁰Po/²¹⁰Pb activity ratio. The first method simply consists in dividing ²¹⁰Po activity by ²¹⁰Pb activity. It is independent from gross alpha/beta measurements but it implies a correction for ²¹⁰Po (see section 2.4). Since this correction relies on the value of ²¹⁰Pb activity determined by gamma spectrometry with high uncertainty owing to low counting statistics, the corrected ²¹⁰Po 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 ²¹⁰Po variation inside the sample. This
assumption will be discussed later in the light of obtained results. The correction formula is
detailed in Appendix B.

221

222 **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 <u>Gross alpha/beta and ²¹⁰Pb activity levels</u>

Gross alpha activity at 5 days was found at a level of $0.016 \pm 0.008 \text{ mBq/m}^3$ (mean and 230 standard deviation), and gross beta activity at 5 days was found at a level of 0.4 ± 0.2 231 mBq/m³ (mean and standard deviation). These levels are consistent with the values usually 232 reported in the RNM. ²¹⁰Pb activity was found at a level of $0.3 \pm 0.2 \text{ mBq/m}^3$, which is in 233 good agreement with monthly averages previously recorded at sites located nearby our 234 sampling site by Bourcier et al. (2011), *i.e.*, from $0.33 \pm 0.10 \text{ mBq/m}^3$ to $1.13 \pm 0.34 \text{ mBq/m}^3$ 235 at the Opme station (5.7 km SSW from our sampling site), and from 0.34 \pm 0.04 mBq/m³ to 236 $1.35 \pm 0.14 \text{ mBq/m}^3$ at the Puy-de-Dôme observatory. 237

3.2 Gross beta activity versus ²¹⁰Pb activity at 5 and 50 days and the excess of gross beta
 activity

Figure 3 displays 5-day beta activities as a function of ²¹⁰Pb activities. A marked 240 correlation between these two activities is found (R^2 =0.98), but ²¹⁰Pb activity is significantly 241 lower than beta activity ($\beta = 1.27 \times {}^{210}$ Pb + 0.05 mBq/m³, best fit). At 50 days, a marked 242 correlation between gross beta and ²¹⁰Pb activities is also found (β = 1.44 × ²¹⁰Pb - 0.02 243 mBq/m³, $R^2 = 0.97$). These excellent correlations at 5 and 50 days mean that ²¹⁰Bi coming 244 from ²¹⁰Pb decay is the main source of long-lived beta radioactivity of atmospheric aerosols 245 (*i.e.*, still present in the filter 5 days after sampling), in good agreement with previous studies 246 (e.g., Mattsson et al., 1996). However, obtained linear coefficients are significantly higher 247 than 1 meaning that gross beta activity is in excess compared to ²¹⁰Pb activity. As stated 248 previously, gross beta activity might underestimate ²¹⁰Bi activity and therefore this excess 249 cannot be due to a calibration bias (if such a bias exists). At 5 days, ²¹⁰Bi activity could be 250 higher than 210 Pb activity but this possibility can likely be discarded since 210 Bi/ 210 Pb activity 251 ratio is generally < 1 in tropospheric air with a typical value of 0.5 (Poet et al., 1972). 252 Moreover, at 50 days, when ²¹⁰Pb and ²¹⁰Bi are in radioactive equilibrium, the clear 253 discrepancy observed between gross beta and ²¹⁰Pb activities proves that long-lived 254 radionuclides different from ²¹⁰Pb contribute to gross beta activity. Assuming that calibration 255 256 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 257 210 Pb- 210 Bi equilibrium activity is 0.1 mBq/m³ (with a standard deviation of ± 0.1 mBq/m³). 258 Could such an excess be explained by the presence of other beta emitters like 40 K, 32 P, 33 P, or 259 35 S ? 40 K activity was not detected by gamma spectrometry for any sample in this study and 260 detection thresholds were typically higher than 0.1 mBq/m³ (1.4 ± 0.7 mBq/m³, mean and 261

standard deviation of detection thresholds). However, ⁴⁰K activity levels measured at the 262 nearby Opme station (5.7 km SSW from our sampling site) (OPERA-AIR network) in the 263 period March 2017-June 2018 are significantly lower than 0.1 mBq/m³ with an average value 264 of 6.2 \pm 3.2 μ Bq/m³ (Olivier Masson, unpublished data). Even if some episodic events with 265 high ⁴⁰K atmospheric activities (Hernández et al., 2005) cannot be ruled out, these low-level 266 measurements suggest that ⁴⁰K cannot be the main beta emitter contributing to the 267 observed excess. ³²P, ³³P, and ³⁵S are pure beta emitters and therefore they cannot be 268 measured by gamma spectrometry. However, the order of magnitude of airborne activity 269 levels reported in the literature for ³²P, ³³P and ³⁵S (Lal and Suess, 1968; Lujanien et al., 1997) 270 is about 0.1 mBq/ m^3 . When summed up, the activities of cosmogenic radionuclides might 271 exceed the observed excess of beta activity ($\sim 0.1 \text{ mBq/m}^3$). Nevertheless, the beta detection 272 yield of ³³P and ³⁵S with a gross alpha/beta counting device might be very small due the low 273 274 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 275 that the observed beta excess is compatible with a contribution of cosmogenic 276

277 radionuclides.

278

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 ²¹⁰Pb 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

282 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 (³²P), 25.4 days (³³P) and 87.3 days (³⁵S). Therefore, their activity in the filter
- significantly decreases between 5 and 50 days.

In order to check whether the decrease of ³²P, ³³P and ³⁵S 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 ²¹⁰Pb) using the following equation:

$$\tau_{app} = \frac{-\Delta t \ln 2}{\ln \frac{\beta_{50} - {}^{210} \text{Pb}}{\beta_5 - {}^{210} \text{Pb}}}$$

289

(eq. 1)

where Δt corresponds to the interval between 5-day and 50-day analyses and eta and 210 Pb 290 correspond to gross beta activity and ²¹⁰Pb activity, respectively. This calculation is 291 illustrated on figure 4b. Values of τ_{app} calculated for the ten samples acquired in 2017 range 292 from 30 to 1500 days with a median value of 80 days and mean value of 271 days (one 293 294 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, τ_{app} must be 295 considered as a maximum estimate of the beta excess half-life since the increase in ²¹⁰Bi 296 297 activity between 5 and 50 days could partially counter-balance the activity decrease of shortlived cosmogenic radionuclides. Indeed, ²¹⁰Bi activity is generally lower than ²¹⁰Pb in the 298 troposphere (see above), therefore the activity of ²¹⁰Bi in the filter gradually increases until 299 radioactive equilibrium is reached with ²¹⁰Pb after about one month. 300

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 ³²P-³³P-³⁵S/²¹⁰Pb activity ratios and/or a ²¹⁰Bi/²¹⁰Pb initial activity ratio closer to 1 (smaller ²¹⁰Bi build-up).

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

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310 3.4 <u>Gross alpha activity versus ²¹⁰Po activity at 50 days</u>

Figure 5 compares 50-day gross alpha activity and ²¹⁰Po activity. Reported polonium 311 activities are corrected for the build-up taking place between the gross alpha/beta counting 312 at 50 days and ²¹⁰Po measurement 10 to 20 days after (see methods for more details). 313 Uncertainties are calculated by quadratic propagation of ²¹⁰Po measurement uncertainty 314 and ²¹⁰Pb activity uncertainty (used for the correction, see appendix A). An excellent linear 315 correlation between the two activities is found (R^2 = 0.99) and gross alpha activity at 50 days 316 is lower than ²¹⁰Po activity (best fit: $\alpha = 0.83 \times {}^{210}$ Po mBq/m³, mean ratio of 0.72). Linear 317 correlation between the two activities strongly suggests that ²¹⁰Po is the main source of 318 alpha activity at 50 days. This is in agreement with previously reported activity levels of only 319 $0.5-1 \mu Bq/m^3$ for long-lived alpha emitters in the atmosphere (²³⁸U, ²³⁰Th, ²²⁶Ra, ²³²Th, ²²⁸Ra, 320 ²²⁸Th) ("Sources and effects of ionizing radiation", UNSCEAR 2008 Report, 2010 and 321 references therein). The fact that alpha gross alpha activity is smaller than ²¹⁰Po activity can 322 be explained by the measurement process and alpha particles self-absorption in the filter 323 (see discussion). 324

325

3.5 Gross alpha activity at 5 days versus build-up corrected ²¹⁰Po activity

Figure 6a represents gross alpha activity measured at 5 days as a function of build-up corrected 5-day ²¹⁰Po activity (see methods). In marked contrast with the situation at 50 days, gross alpha and ²¹⁰Po activities are poorly correlated ($R^2 = 0.77$ for 2017 samples and $R^2 = 0.78$ for 2018 samples), even though positive correlation trends are still observed. 330 Interestingly, even if correlation coefficients are similarly low for 2017 and 2018, the 2018 samples group (characterized by a shorter time lag before ²¹⁰Po measurement) present a 331 mean alpha/²¹⁰Po ratio closer to the mean ratio found for 50-day activities (5-day ratios of 332 0.66 for 2018 samples and 0.4 for 2017 samples, to be compared to the 50-day ratio of 0.72). 333 Moreover, the uncertainty on build-up corrected ²¹⁰Po activity is much higher for the 2017 334 sample group than for the 2018 sample group (see figure 6a). Since the 5-day $alpha/^{210}$ Po 335 ratio has no obvious reason to change between 2017 and 2018 and since ²¹⁰Po is the 336 outstanding contributor of long-lived alpha radioactivity (see figure 1), these observations 337 suggest that the correction applied to ²¹⁰Po activity in order to recalculate its value backward 338 in time introduces an important dispersion and bias in the corrected values, especially when 339 the correction lag is long (2017 sample group). Therefore, obtained ²¹⁰Po corrected activities 340 cannot be trusted as representative of ²¹⁰Po atmospheric level for 2017 samples. 341 Contrastingly, the good agreement between 5-day $alpha/^{210}$ Po ratio of 2018 samples and the 342

343 50-day ratio suggests that corrected 210 Po activities are not significantly biased.

344 <u>3.6 Atmospheric ²¹⁰Po/²¹⁰Pb activity ratio inferred from gross alpha activity variation</u> 345 (2017 samples)

Due to large uncertainty propagation on corrected ²¹⁰Po activity using the ²¹⁰Pbbased approach (see section 3.5), we attempted to determine ²¹⁰Po/²¹⁰Pb 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 ²¹⁰Po 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

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

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

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

Using the same method, we computed the 5-day 210 Po/ 210 Pb ratio for each sample (taking into account the exact time lag between sampling and 5-days analysis) and derived the 5-day 210 Po activity (multiplying by 210 Pb activity) that we compared to 5-day gross alpha activity (figure 6b). A much better correlation is found as compared to that of the other method (R²= 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/²¹⁰Po ratio found at 50 days.
These results confirm that the alpha/²¹⁰Po ratio might not significantly change between 5
days and 50 days, and demonstrates that ²¹⁰Po is the dominant long-lived alpha emitter of
atmospheric aerosols.

380

381

3.7 <u>Atmospheric ²¹⁰Po/²¹⁰Pb activity ratio versus gross alpha/beta activity ratio</u>

Figure 8 represents gross alpha/beta activity ratio measured at 5 days as a function of 382 atmospheric 210 Po/ 210 Pb activity ratio inferred from gross alpha activity variation (2017) 383 samples) and from corrected ²¹⁰Po activity (2018 samples). The two activity ratios are not 384 well correlated (R^2 = 0.12 and 0.46 for 2017 and 2018 respectively). Gross alpha/beta activity 385 ratio is lower than 210 Po/ 210 Pb activity ratio by a mean factor of 0.9 (2017) or 0.6 (2018). 386 Lower alpha/beta activity ratio as compared to 210 Po/ 210 Pb activity ratio is logical since 5-day 387 gross beta activity overestimates ²¹⁰Pb activity (see section 3.2) and since alpha activity 388 underestimate ²¹⁰Po activity (see section 3.4). Thus, both differences tend to an 389 underestimation of ²¹⁰Po/²¹⁰Pb activity ratio by the alpha/beta activity ratio. However, it 390 should be pointed out that both ratios are almost always compatible considering the large 391 error bars, especially for the 210 Po/ 210 Pb activity ratio. Actually, gross alpha/beta activity 392 ratio has a typical relative uncertainty of 22% \pm 14% (k=2) while ²¹⁰Po/²¹⁰Pb ratios present 393 larger relative uncertainties ($36\% \pm 2\%$ in 2018 and $50\% \pm 20\%$ in 2017). For both kinds of 394 ratio, the relative variability of the sample set (2o standard deviation divided by mean) is not 395 considerably higher than measurement uncertainties (48% for alpha/beta ratio and 70% for 396 210 Po/ 210 Pb ratio). 397

398

3.8²¹⁰Po levels in France

Based on the estimate of atmospheric ²¹⁰Po/²¹⁰Pb activity ratio and on measured ²¹⁰Pb activities, it is possible to determine the airborne ²¹⁰Po activity level at the study site. We find a level of ²¹⁰Po of $13 \pm 6 \,\mu$ Bq/m³ (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 μ Bq/m³) and constitutes the first chronicle of ²¹⁰Po activity in France.

404

405 **4. Discussion**

406 <u>4.1 Origin and consequences of the gross beta activity excess compared to ²¹⁰Pb</u>

Gross beta activity is found in marked excess as compared to ²¹⁰Pb activity by a typical 407 factor of ~1.3 (see section 3.2). This excess is higher at 5 days than at 50 days after sampling 408 and can be attributed to the presence of short-lived cosmogenic radionuclides (see sections 409 3.2 and 3.3). This factor can serve as a correction factor to retrieve ²¹⁰Pb activity from 5-day 410 gross beta activity. However, it is interesting to point out that a previous comparison study 411 (based on a larger set of samples) did not identify this phenomenon (Mattsson et al., 1996). 412 The authors found a regression equation equivalent to β = 1.03 × ²¹⁰Pb + 0.02 mBq/m³ (see 413 414 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 415 activity excess compared to ²¹⁰Pb (and the correction factor to apply) may depend on the 416 location and on the potential presence of local sources of other beta emitters. As a 417 consequence, the use of gross beta activity to infer ²¹⁰Pb activity might be cautious and 418 requires a calibration of gross beta activity vs ²¹⁰Pb to be made on site, for instance using the 419 protocol presented in this study. If such a calibration of gross beta activity vs ²¹⁰Pb activity 420

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.

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

428

4.2 Alpha particles self-absorption in filters

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

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

449

450 <u>4.3 Advantages and disadvantages of ²¹⁰Po measurement strategies in atmospheric</u>
451 <u>samples</u>

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

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

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

490 be detected since an excellent correlation is found between the two activities. However, short-lived radionuclides with significant initial activity compared to ²¹⁰Po could have 491 completely decayed and could be missed at 50 days. Such radionuclides would likely have a 492 half-life shorter than ~10 days. Conversely, they must have a half-life > ~1 day to be still 493 active in the sample at 5 days (this is not the case for all radon and thoron daughters). A 494 495 search in a radionuclide database indicates that potential candidates for naturally occurring alpha-emitters with a half-life between 1 and 10 days are ²²³Ra and ²²⁴Ra. For both nuclides, 496 we found no atmospheric activity reported in the literature. However, airborne 228 Th (224 Ra 497 father in the ²³²Th decay chain) activity has occasionally been reported to be about $1 \mu Bq/m^3$ 498 (Kolb, 1989). Therefore we suggest that ²²⁴Ra activity level is in the same order of magnitude 499 500 due its short half-life (3.6 days). Such level is very low compared to the amplitude of gross alpha activity variation (tens of μ Bq/m³) and would not affect the final result. Because ²²³Ra 501 originates from the 235 U decay chain, which is much less abundant than 232 Th and 238 U in 502 nature (0.7% of uranium and Th/U = 4.2), we suggest that 223 Ra levels in the atmosphere are 503 likely to be even lower than ²²⁴Ra levels. Therefore, it appears that the initial assumption 504 lying behind the method is robust. 505

506 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 507 determination is long (typically 50-70 days). Conversely, if the time lag is short (10-20 days) 508 the two methods give similar results, even if the typical relative uncertainty is higher for the 509 gross alpha activity variation method as compared to direct ²¹⁰Po determination (50% 510 compared to 35%). Since both methods are based on measured ²¹⁰Pb activity, it should 511 finally be noted that the uncertainty of both methods would decrease if a more precise ²¹⁰Pb 512 activity measurement is available. 513

514

<u>4.4 Alpha/beta activity ratio versus 210 Po/ 210 Pb activity ratio and the detection of </u>

515 <u>extreme natural events</u>

5-day alpha and beta activities are routinely measured in many locations for 516 monitoring reasons. Thus, large databases of alpha/beta activity ratio are available and could 517 be used to study ²¹⁰Po and ²¹⁰Pb in the atmosphere. When comparing this ratio with our 518 estimates of 210 Po/ 210 Pb activity ratio, we found that both ratios match each other due to 519 520 large uncertainties. Due to the rather low number of samples (16) and to the fact that ²¹⁰Po/²¹⁰Pb and gross alpha/beta ratio variability did not significantly exceed the 521 measurement uncertainty, it is not possible to conclude about the correlation between the 522 two ratios. However, when looking at mean ratios, our data suggest that alpha/beta activity 523 ratio is smaller than 210 Po/ 210 Pb activity ratio. This underestimation is potentially due to two 524 phenomena: (i) presence of other beta emitters leading to an overestimation of ²¹⁰Pb by 525 gross beta activity and (ii) calibration error on alpha measurement due to an inappropriate 526 treatment of alpha self-absorption in the filter, leading to underestimation of ²¹⁰Po by gross 527 528 alpha activity.

The amplitude of these two biases has been determined in sections 3.2, 3.4, 3.5 and 3.6. 529 Considering the mean and standard deviation of $alpha/^{210}$ Po ratios (see figures 5 and 6a, b) 530 531 determined at 5 and 50 days with different methods, it is possible to infer a typical $alpha/^{210}$ Po ratio of 0.7 with a sample-to-sample variability of 15%. At 5 days, the beta/ 210 Pb 532 ratio has a mean value of 1.5 with a variability of 15%. Thus, it is possible to infer a typical 533 factor of 0.5 between gross alpha/beta and 210 Po/ 210 Pb activity ratios with a 1 σ variability of 534 20%. Consequently, the gross alpha/beta activity ratio appears to be suitable for tracking 535 relative ²¹⁰Po/²¹⁰Pb ratio variations much larger than 20% (*i.e.* at least 100%). Yet, relative 536

537	variations of ²¹⁰ Po activity associated with savanna fire plumes or volcanic plumes often									
538	exceed this threshold as reported by several authors (e.g., Le Cloarec et al., 1995; Nho et al.,									
539	1996, 1997). Therefore, the gross alpha/beta ratio might be able to record such variations.									
540	Finally it is possible to imagine a protocol dedicated to the monitoring of these extreme									
541	natural events:									
542	- The protocol is triggered on when 5-day alpha/beta ratio is 100% larger than the									
543	reference value.									
544	- A gamma spectrometry is performed as long as possible to obtain ²¹⁰ Pb activity in									
545	the sample.									
546	- If possible, an aliquot is analysed as soon as possible for ²¹⁰ Po determination.									
547	- In any case, several gross alpha/beta countings are performed during 50 days to									
548	better constrain the initial 210 Bi/ 210 Pb and 210 Po/ 210 Pb ratios and the cosmogenic									
549	radionuclides.									
550										
551	5. Conclusion									
552	Gross alpha/beta activity and specific 210 Po and 210 Pb activity measurements have been									
553	performed on a set of atmospheric aerosols samples in order to investigate co-variations of									
554	554 these different activities. Several main conclusions can be drawn:									
555	- Beta activity was found to systematically overestimate 210 Pb activity by ~30%.									
556	Using 5 and 50-day gross beta activity measurements, it is possible to constrain									
557	the nature of this beta activity excess. We show that it is mostly due to short-									
558	lived beta emitters (³³ P, ³² P, and ³⁵ S).									

50 - 50-day gross alpha activity is mainly due to ²¹⁰Po. However, alpha activity is found
 to underestimate ²¹⁰Po 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.

564

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

570

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

576

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

583

584 - A first estimation of atmospheric ²¹⁰Po activity level in France is $13 \pm 6 \mu Bq/m^3$.

587 APPENDIX A: correction of ²¹⁰Po build-up in the filter.

²¹⁰Po activity measured at a given time *t* must be corrected to take into account the build-up of this radionuclide by ²¹⁰Bi decay in the sample. The formula of this correction can be obtained by solving the decay equations for a three-member chain $(1\rightarrow 2\rightarrow 3, \text{ or}$ ²¹⁰Pb \rightarrow ²¹⁰Bi \rightarrow ²¹⁰Po). 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:

594
$$A_{i}(t) = A_{i,0}e^{-\lambda_{i}t} + \sum_{m=1}^{i-1}A_{m,0}\prod_{q=m+1}^{i}\lambda_{q}\sum_{k=m}^{i}\frac{e^{-\lambda_{k}t}}{\prod_{j=m}^{i}(j\neq k)}(\lambda_{j}-\lambda_{k})}$$

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), λ_i for the decay constant of i and t for the time. In the case of ²¹⁰Pb -> ²¹⁰Bi -> ²¹⁰Po (1->2->3) decay chain, the equation A.1 translates to:

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

599 (eq. A.2)

600 where $(X)_0$ is the activity of the aliquot at a given initial time and $(X)_t$ is the activity of the 601 same aliquot after a time t (X corresponding either with ²¹⁰Pb, ²¹⁰Bi or ²¹⁰Po, the 210 602 exponent is not reproduced in the equation for simplicity). C_X^t is a numerical coefficient that 603 is a function of time t and of radioactive decay constants of ²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po:

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

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

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

604

607

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

605 Using this formalism it is possible to infer initial polonium content of the sample using the606 following equation:

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

(eq. A.6)

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

$$(Po)_{0} = \frac{(Po)_{t}}{C_{Po}^{t}} - \frac{(Pb)_{0}C_{Pb}^{t}}{C_{Po}^{t}} \left(1 + \frac{(Bi)_{0}}{(Pb)_{0}}\frac{C_{Bi}^{t}}{C_{Pb}^{t}}\right)$$
(eq. A.7)

615

616 We can neglect the contribution of ²¹⁰Bi initial activity if it is smaller than the ²¹⁰Pb term 617 contribution, in other words if:

$$\frac{(\mathrm{Bi})_{0}}{(\mathrm{Pb})_{0}}\frac{C_{\mathrm{Bi}}^{t}}{C_{\mathrm{Pb}}^{t}} \ll 1$$

618

619First, C_{Bi}^t/C_{Pb}^t is about 10% for t = 50 days. Second, ${}^{210}Bi/{}^{210}Pb$ activity ratio of atmospheric620aerosols is generally reported lower than 1 with a mean value of 0.5 (e.g. Poet et al., 1972).621Therefore, it is likely that the contribution of the ${}^{210}Bi$ term in equation 4 is no more than 10622% of the contribution of ${}^{210}Pb$, and likely around 5 %. Because the typical uncertainty on623 ${}^{210}Pb$ values measured by gamma spectrometry is larger than 10 % (see table 1), it is624legitimate to neglect ${}^{210}Bi$ initial activity in the correction formula. Equation A.7 can thus be625simplified as:

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

626

(eq. A.9)

(eq. A.10)

Finally, the uncertainty of corrected 210 Po activity is obtained by convolution of the uncertainties of 210 Po and 210 Pb measurements:

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

629

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

631

632

633

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

637 Supposing that gross alpha activity relative variation between 5 and 50 days is only 638 due to ²¹⁰Po, we can write:

$$\frac{\alpha_{50} - \alpha_5}{\alpha_5} = \frac{(\text{Po})_{50} - (\text{Po})_5}{(\text{Po})_5}$$
(eq. B.1)

639

640 where α and $(Po)_t$ correspond to gross alpha activity and ²¹⁰Po activity respectively (either 641 at 5 or 50 days). Replacing right terms of equation B.1 by their expression given by equation 642 A.2, the relative variation of gross alpha activity becomes:

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

643

644 where $\Delta C_{\rm X} = C_{\rm X}^{50} - C_{\rm X}^{5}$. Dividing by (Po)₀ and using the notation R_0 for ²¹⁰Po/²¹⁰Pb initial 645 activity ratio, equation B.2 becomes:

$$\frac{\alpha_{50} - \alpha_5}{\alpha_5} = \frac{\Delta C_{\rm Pb} R_0^{-1} + \Delta C_{\rm Bi} (\rm Bi/Pb)_0 R_0^{-1} + \Delta C_{\rm Po}}{C_{\rm Pb}^5 R_0^{-1} + C_{\rm Bi}^5 (\rm Bi/Pb)_0 R_0^{-1} + C_{\rm Po}^5}$$
(eq. B.3)

(eq. B.2)

646

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 δ :

$$R_{0} = \frac{C_{Pb}^{5}\delta - \Delta C_{Pb} + \left(\frac{Bi}{Pb}\right)_{0} \left(C_{Bi}^{5}\delta - \Delta C_{Bi}\right)}{\Delta C_{Po} - C_{Po}^{5}\delta}$$

(eq. B.4).

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

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

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Figures and tables

Table 1: Sampling details and analysis results. All uncertainties are given with a coverage factor k=2. ²¹⁰Po activity is given at the time of ²¹⁰Po

deposition onto plates. All activities are expressed in mBq/m³ considering sampled volumes and a constant aliquot/filter surface ratio of 0.3.

	Sampling start	Sampling duration	Sampled volume	Dust load	1st gross alpha/beta counting	Gross activity 5 days (mBq/m3)		2 nd gross alpha/beta Gross counting		vity 50 days q/m³)	²¹⁰ Pb activity (mBq/m3)	²¹⁰ Po meas. delay (d)	²¹⁰ Po activity (mBq/m³)
Sample	(local time)	(h)	(m³)	(µg/m³)	delay (d)	alpha	beta	delay (d)	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	$0,09 \pm 0,01$
2	4/4/17 11:33	73,8	11073	15	5	0,008 ± 0,002	0,203 ± 0,007	63	0,032 ± 0,003	$0,178 \pm 0,007$	$0,16 \pm 0,04$	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	$0,31 \pm 0,02$	0,21 ± 0,03	110	$0,11 \pm 0,01$
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	$0,16 \pm 0,02$	71	0,067 ± 0,007
5	21/4/17 13:53	71,6	10742	10	10	0,020 ± 0,003	$0,48 \pm 0,01$	56	$0,069 \pm 0,004$	$0,39 \pm 0,01$	0,30 ± 0,03	65	$0,10 \pm 0,01$
6	2/5/17 12:54	45,9	6893	6	5	0,004 ± 0,003	$0,180 \pm 0,008$	53	$0,018 \pm 0,003$	$0,138 \pm 0,008$	0,09 ± 0,02	82	0,045 ± 0,005
7	12/5/17 18:02	63,3	9485	5	4	0,007 ± 0,002	$0,162 \pm 0,007$	56	0,025 ± 0,003	$0,160 \pm 0,007$	$0,10 \pm 0,02$	71	0,038 ± 0,005
8	23/5/17 13:45	51,9	7781	12	6	0,013 ± 0,003	$0,39 \pm 0,01$	56	0,069 ± 0,005	$0,39 \pm 0,01$	0,27 ± 0,03	69	$0,10 \pm 0,01$
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	$0,147 \pm 0,007$	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	$0,91 \pm 0,02$	112	$0,30 \pm 0,01$	$1,05 \pm 0,03$	0,68 ± 0,06	118	$0,35 \pm 0,04$
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	$0,37 \pm 0,01$				0,22 ± 0,04	21	$0,030 \pm 0,003$
16	21/9/18 16:14	64,3	9631	6	19	0,015 ± 0,002	0,248 ± 0,008				$0,12 \pm 0,03$	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 ²²²Rn daughters have half-lives considerably smaller than 5 days. Contrastingly, most ²²⁰Rn daughters (from the ²³²Th chain) are part of the progeny of ²¹²Pb which has a 10.64 hours half-life. Therefore, the long-lived radioactivity can only be measured after 5 days when ²¹²Pb has thoroughly decayed out (5 days corresponds with eleven ²¹²Pb periods and a 2000 fold reduction of the initial activity). This long-lived radioactivity comes from three different types of radionuclides: long-lived ²²²Rn daughters (²¹⁰Pb, ²¹⁰Bi, ²¹⁰Po), radionuclides of cosmogenic origin (³²P, ³³P, ⁷Be, ³⁵S, ²²Na) and "primordial" radionuclides (⁴⁰K, ²³⁸U, ²³²Th) injected in the atmosphere upon soil erosion. Long-lived alpha activity is largely dominated by ²¹⁰Po. ²¹⁰Pb is the most active long-lived beta emitter but other radionuclides are also significant (³²P, ³³P, ³⁵S, ⁴⁰K).



Figure 2: Activities recorded for all samples in 2017 (a) and 2018 (b), including 5 and 50-day gross alpha/beta activities, ²¹⁰Pb activity measured by gamma spectrometry and ²¹⁰Po activity measured by alpha spectrometry after chemical separation (activities reported on the graph are not corrected for ²¹⁰Po 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 ²¹⁰Pb 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 ²¹⁰Pb 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 ²¹⁰Pb activity at 5 days (y axis) and at 50 days (x axis). Error bars are calculated taking into account gross beta activity uncertainty only. Isoligns 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 ²¹⁰Po 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 ²¹⁰Po activity recalculated at t = 5 days using different approaches: (a) build-up correction of ²¹⁰Po activity (see appendix A for calculation details) and (b) determination of ²¹⁰Po/²¹⁰Pb activity ratio from gross alpha activity variation between 5 and 50 days (see appendix B for calculation details). For each

method, the mean alpha/²¹⁰Po activity ratio is plotted (coloured lines) and compared to the alpha/²¹⁰Po measured at 50 days (0.83, black line). All uncertainties are propagated to the corrected ²¹⁰Po activity. Moreover, mean and standard deviation of alpha/²¹⁰Po 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 ²¹⁰Po/²¹⁰Pb 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 ²¹⁰Po activities divided by ²¹⁰Pb 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 ²¹⁰Bi/²¹⁰Pb 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). ²¹⁰Po/²¹⁰Pb activity ratio determined from corrected ²¹⁰Po activity and ²¹⁰Pb activity are plotted with error bars corresponding to the uncertainty (k=2) on ²¹⁰Po 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.