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Analysis of ^7Be and ^{210}Pb concentration and $^7\text{Be}/^{210}\text{Pb}$ activity ratio in ground level air in Palermo (Italy)

Recto running head : RADIATION EFFECTS AND DEFECTS IN SOLIDS

Verso running head : S. BASILE ET AL.

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ABSTRACT

A series of measurements of particulate samples collected on paper filters in Palermo (Italy) during 1995–2005 has been performed to detect ^{210}Pb air activity concentration and, along with previous similar data on ^7Be , to evaluate their activity ratio. Average values for the daily activity concentrations of ^7Be and ^{210}Pb are found to be 4.7 and 0.6 mBq m^{-3} , respectively, 9.8 being the average activity ratio. Data confirm a seasonal behavior for both radionuclides. A correlation between ^7Be and ^{210}Pb air activity concentrations seems to exist, despite their different origins. The time behaviors of both ^7Be and ^{210}Pb air concentrations and $^7\text{Be}/^{210}\text{Pb}$ activity ratio have been compared with some meteorological parameter time series. The analysis of the data shows a weak correlation with rainfall, while no correlation can be established with other parameters. Monthly and weekly average values have been reconstructed taking into account missing data, in order to carry out homogeneous comparisons with available data from other geographical areas. Data series correlations and the frequency analysis show the importance of atmospheric transport processes and the influence of meteorological and climatic parameters (in particular rainfall) in determining the concentrations in air of both radionuclides.

Keywords

^7Be ; ^{210}Pb ; activity concentration; air particulate; Palermo

1. Introduction

A renewed interest on using radioactive tracers to study transport and mixing processes in the atmosphere has raised in recent times. ^7Be and ^{210}Pb have assumed an ever-increasing importance among the most commonly used radioactive tracers in the atmosphere. Both radionuclides are commonly used radiotracers in transport and mixing in air processes studies and can be very useful for differentiating the sources of air masses that reach a given measurement site, as also pointed out in some recent works

(1,2). Beryllium-7 is the product of the interaction of cosmic rays with Nitrogen and Oxygen nuclei. Its cosmogenic origin makes the measured concentrations strongly dependent on the geographical position and seasonal cycles. It emits 478 keV gamma photons and has a half-life of about 53 days. Once produced, it is mixed and deposited gradually until it reaches the closest to the ground earth atmosphere layers. Lead-210 (half-life 22.3 years) is instead a decay product of the radioactive family of the ^{238}U . The specific activities of this radionuclide are therefore strongly dependent on the detection site. Once produced in the atmosphere, the ^{210}Pb is rapidly fixed by sub-micrometric dimension aerosol particles with which it has a particular affinity. Since the half-life is much longer than the residence time of the aerosol, it is particularly useful for studying the transport over large distances and the removing particulate matter from the atmosphere processes. Its 46.5 keV gamma emission makes it necessary to use a detector suitable for low gamma-ray energies. Beryllium-7 air activity concentration measurements were already performed in the period 1982–2004 through gamma-ray spectrometry of air particulate samples collected on paper filters by means of an high volume sampler (3–5). Lead-210 air activity measurement was performed on some samples using spectrometric systems based on *p*-type HPGe (High-Purity Germanium) detectors (6). ^{210}Pb activity measurements were again performed on the samples collected during the period 1995–2005, thanks to the availability of a planar HPGe detector, with a good efficiency for the direct measurement of the 46.5 keV gamma emission (7). In this way, looking at the time interval of joint availability of concentration data (1995–2004), an analysis has been performed in order to highlight possible correlations between the two radionuclides and local weather and climate data, and to study the behavior of the activity ratio. In this paper, a statistical analysis of the data has been carried out, taking into consideration the time series (integrating them for the missing data) of monthly and weekly average values in order to make homogeneous comparisons with available data from other geographical areas. The correlations between the data series for the two radionuclides have been investigated and the frequency analysis has been carried out in order to highlight seasonal cycles. The results show the importance of the processes of transport into the atmosphere and the influence of the meteorological and climatic parameters (in particular rainfall) to determine the concentrations in the air of the aforementioned radionuclides.

2. Materials and methods

Particulate collection was performed by suction of atmospheric air through $45\text{ cm} \times 45\text{ cm}$ Sofiftra Poelman HYN-75 (Bleu type) cellulose filter paper using a high-volume air sampler located on the roof of our department, 20 m above ground level. The sampling time for all the particulate samples was 14 h from 6 pm to 8 am on the next day. The filtered air volume is typically about 10,000–12,000 m^3 . After particulate sampling, the filters were sprayed with a suitable fixer, cut into strips, folded and pressed into $6\text{ cm} \times 6\text{ cm}$ side and 0.7 cm thickness packets by a 15-ton press. These samples are referred to as 'packet-samples' (3–6). A coaxial ORTEC GEM18180 detector with 18% relative efficiency, 2 keV FWHM at 1332 keV was mainly used for ^7Be activity measurements. The same samples were also measured by a GLP Series Planar Low-Energy Photon Spectrometer (LEPS), 1000 mm^2 active area and 7 mm depth, 0.254 mm thick beryllium window, to determine ^{210}Pb activities. The energy resolution (FWHM) was 440 eV at 5.9 keV and 620 eV at 122 keV. The electronic equipment associated with each detector consist generally of an ORTEC 672 amplifier and an ORTEC 919E EtherNIM multichannel Buffer connected into an Ethernet environment. The efficiencies of the two systems for ^7Be and ^{210}Pb were previously determined as described in (7–9). Figure 1 shows the shielding (left) and the measurement cavity (right) of the LEPS detector. In order to determine the contribution of the decay of Radon daughters to ^{210}Pb activity on filter, a series of short-term filtrations (1 h at most), was carried out. At the end of the aspiration, the filter was proactively measured to determine the number of atoms of ^{214}Pb and ^{214}Bi present on the filter, and, therefore, the contribution to ^{210}Pb activity on the filter due only to complete decay of Radon daughters.

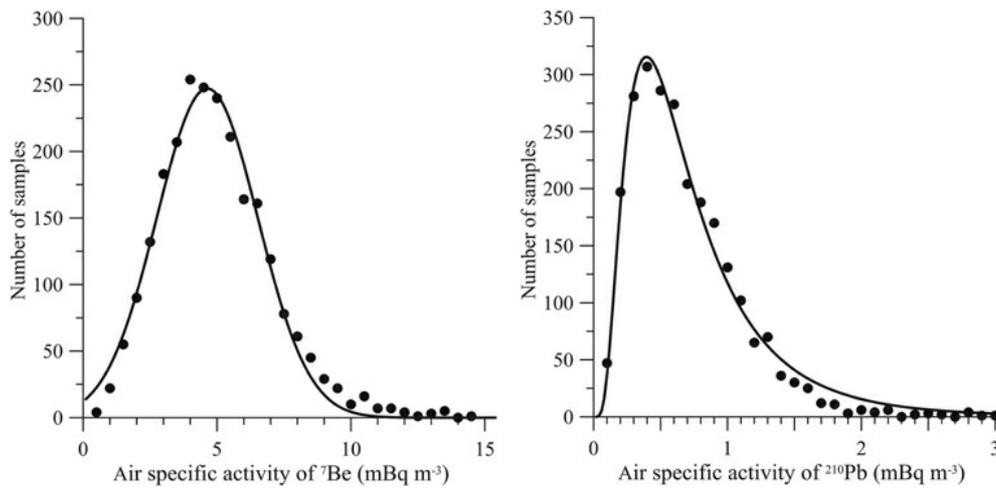
Figure 1. Pictures of the spectrometric system along with the shielding (left) and detail of the measurement cavity filled with OFHC copper (right).



3. Results and discussion

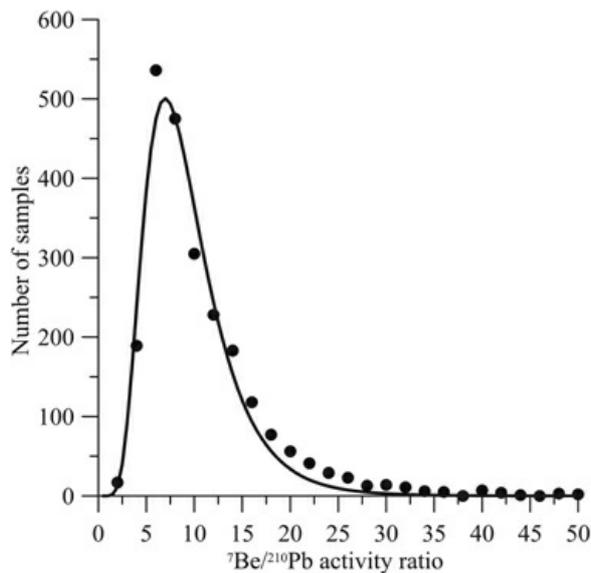
In all the measurements, values of corresponding photopeak count rate for both ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ turned out to be much larger than the detection limit (DL) of the spectrometric analysis systems. This is due to high sampled air volume (about $12,000\text{ m}^3$ in 14 h) and to the use of LEPS detector, particularly suitable to detect 46.5 keV gamma rays of ${}^{210}\text{Pb}$ (6). The spectrometric measurements carried out on the filters of the considered period (1995–2005) allowed to determine the activity of ${}^{210}\text{Pb}$ with a good statistical precision (average value of the standard deviation of the areas of photopeaks about 4%). In order to exclude a possible contribution due to particles containing ${}^{226}\text{Ra}$, which could alter the activity values on the ${}^{210}\text{Pb}$ filter, a region of interest (ROI) of the gamma spectrum was also monitored around the 186.1 keV energy of ${}^{226}\text{Ra}$, without finding values above relative DL in all spectra examined. The daily activity concentration values of ${}^7\text{Be}$ are in the range $0.05\text{--}5.35\text{ mBq m}^{-3}$ and exhibit a Gaussian distribution, as shown in the left part of Figure 2. The monthly averages of ${}^7\text{Be}$ concentrations result in the range $2.37\text{--}10.85\text{ mBq m}^{-3}$, in the same range found by other authors (10–15). As to ${}^{210}\text{Pb}$, the daily activity concentration values range between 0.02 and 3.39 mBq m^{-3} , with a log normal distribution (see right part of Figure 2), whereas the monthly averages of air concentration vary from 0.15 to 2.13 mBq m^{-3} , in agreement with values from the literature (13,16–19).

Figure 2. Frequency density distribution (points) and fitting curves (lines) for ${}^7\text{Be}$ (left, Gaussian fitting, mean value 4.63, $R^2 = 0.993$) and ${}^{210}\text{Pb}$ (right, log-normal fitting, mean value 0.68, $R^2 = 0.970$).



Daily ${}^7\text{Be}$ to ${}^{210}\text{Pb}$ activity ratios varied from 0.08 to 58.2 (with an average value of 9.78), with a few high values observed in connection with low values of ${}^{210}\text{Pb}$ concentration, probably due to particular meteorological conditions. The statistical distribution is fitted by a log-normal curve, as shown in Figure 3.

Figure 3. Frequency density distribution (points) and fitting curves (lines) for ${}^7\text{Be}/{}^{210}\text{Pb}$ activity ratio (log-normal fitting, mean value 9.78, $R^2 = 0.933$).



The partial independence from meteorological conditions for the distribution of ${}^7\text{Be}$ air activity concentrations and its dependence on solar sunspot cycle has been investigated in previous works (3,4).

Figures 4–6 show the time series of the monthly average of ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ air concentration and their activity ratio in the same

time interval.

Figure 4. Average monthly air concentration. Left: ${}^7\text{Be}$ (1995–2004). Right: ${}^{210}\text{Pb}$ (1995–2005).

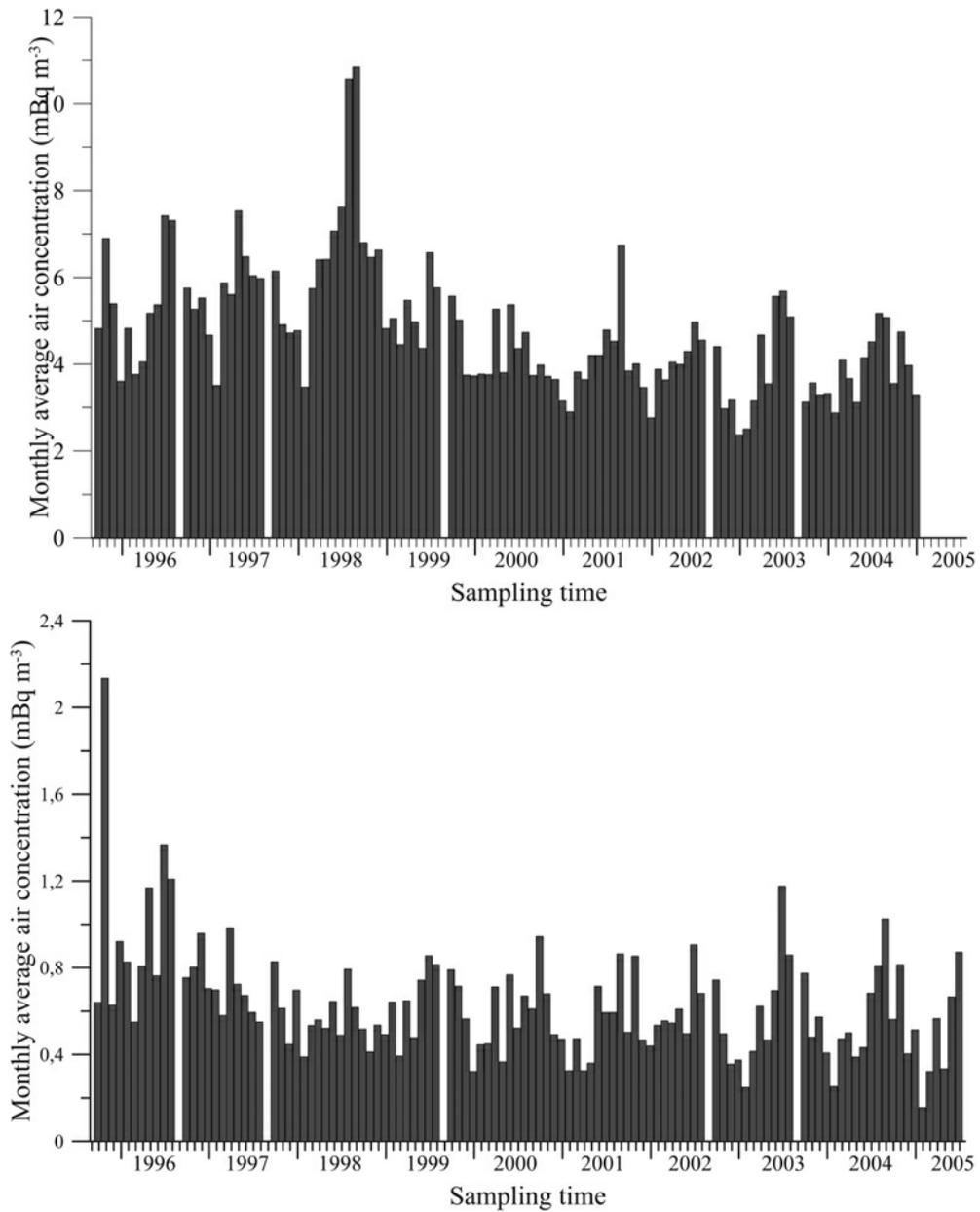


Figure 5. Time series of monthly averaged ${}^7\text{Be}/{}^{210}\text{Pb}$ specific activity ratios (1995–2004).

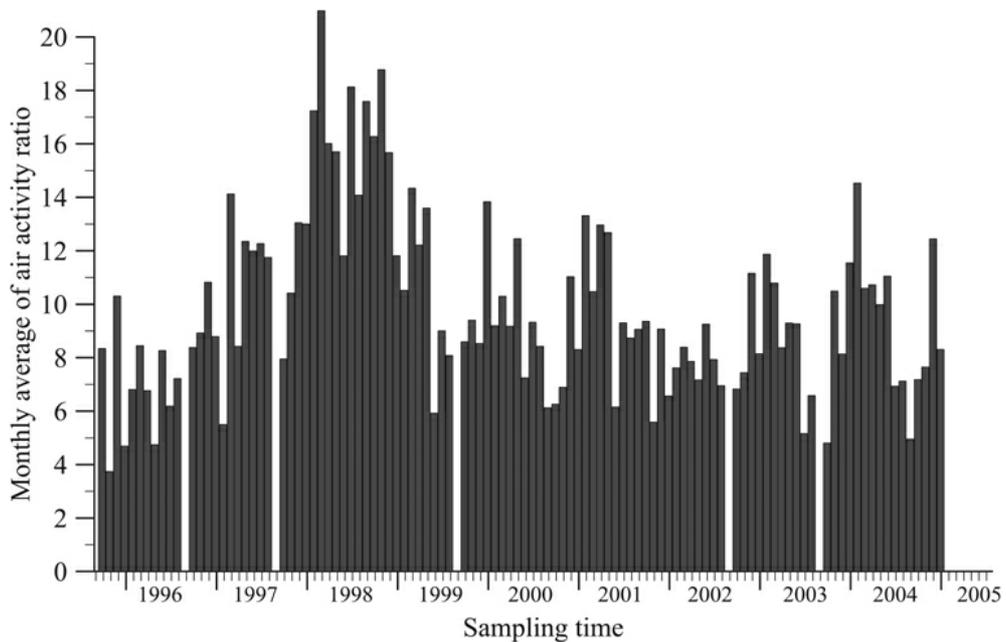
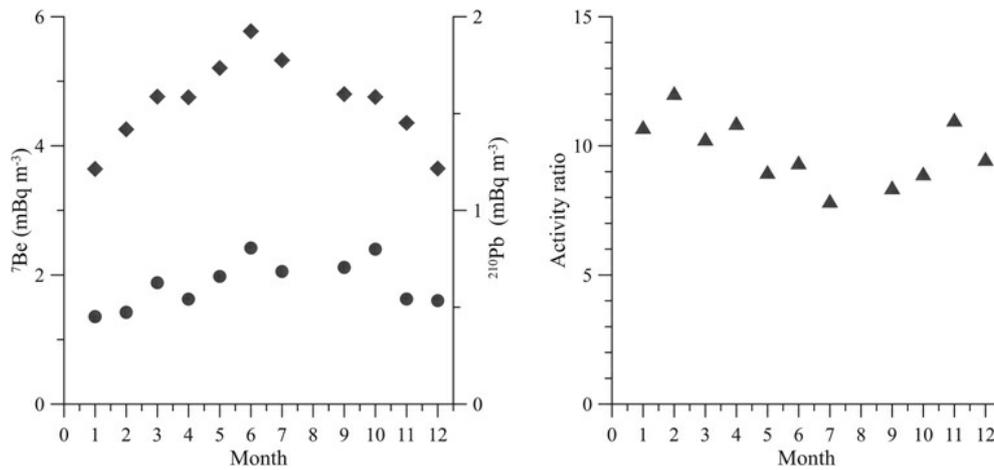


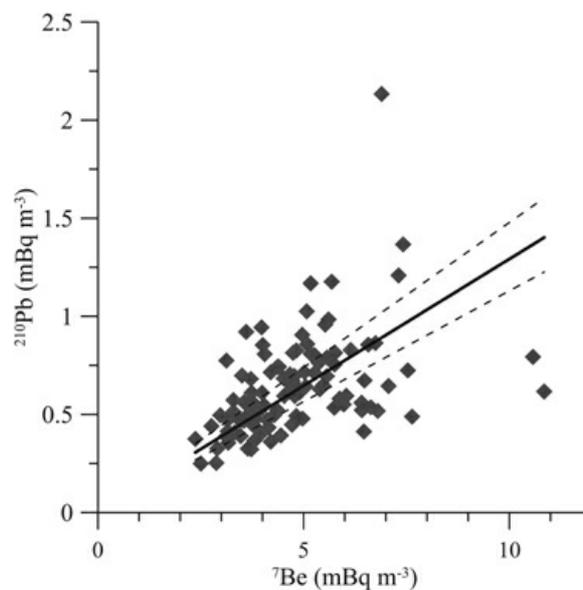
Figure 6. Left: specific activity trends grouped by month for ${}^7\text{Be}$ (diamonds, left vertical axis) and ${}^{210}\text{Pb}$ (circles, right vertical axis). Right: specific activities ratios trend.



In spite of their different origin, a similar seasonal behavior has been observed for both monthly averages of ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ air activity concentrations, with the maximum values detected during late Spring/Summer months (Figure 6, left part). Instead, values of monthly averages of ${}^7\text{Be}/{}^{210}\text{Pb}$ activity ratio indicate an annual trend with higher values in Autumn/Winter months and lower values during warmer months (Figure 6, right part). This is probably due to the characteristics of the sampling site, close to city and campus large buildings and facilities (such as canteen, heating system, student dormitory) that probably contribute partly to the increase of the ${}^{210}\text{Pb}$ in the air in the winter months.

Similarly, a correlation between ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ air activity concentrations has been found, as highlighted in Figure 7 where monthly averages of both ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ air activity concentrations are compared. Because of their different origins, the positive correlation was unexpected and a little surprising. This suggests that the most important factors influencing both radionuclides air concentration behaviors are similar, and probably related to air masses movements (10,12–14,16,18,20–22). Beryllium-7 concentration increasing during warmer months is explained with vertical air mixing and a transport of cosmogenic radionuclides towards low atmospheric layers. The similar increasing on ${}^{210}\text{Pb}$ concentration in Summer/Autumn months can be related, probably, to a recirculation of ${}^{210}\text{Pb}$ deposited on ground surface and not already migrated into the soil. Seasonal variation seems related to temperature change and rain quantity more than pressure change or relative humidity. The correlation between ${}^{210}\text{Pb}$ and ${}^7\text{Be}$ concentrations hints that these two radionuclides could be used as tracers of environmental processes.

Figure 7. ${}^{210}\text{Pb}$ vs. ${}^7\text{Be}$ specific activities. A linear fitting ($R^2 = 0.933$) along with its confidence curves is also shown.

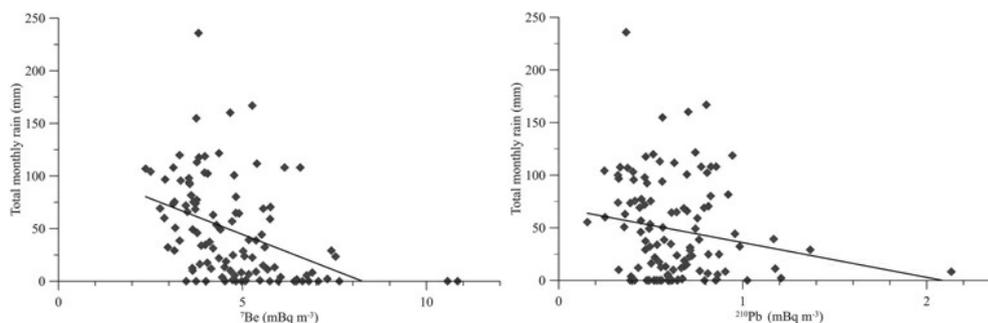


Concerning the possible contribution to ${}^{210}\text{Pb}$ activity on filter due to the decay of Radon daughters, experimental samplings allow to estimate this contribution in a range 2–10%, in comparison with a total ${}^{210}\text{Pb}$ activity on filter variable from 0.3 to 19 Bq. So, this activity does not yield a significant contribution to the air ${}^{210}\text{Pb}$ activity concentration measurements and it can be considered negligible, taking into account the experimental uncertainties (6).

The literature reports studies of correlation with weather and climate parameters (17,23–25). Only a weak correlation with rainfall,

mainly with ${}^7\text{Be}$, can be assessed on a monthly basis, *i.e.* with the total amount of rainfall in the month. As already reported in (4–6) and highlighted in Figure 8, there is a decreasing in the concentrations as the amount of precipitation increases, while the correlation with the average daily temperature appears even weaker. There is no evidence of correlation with relative humidity and the change in atmospheric pressure, while a dependence of the activity of ${}^{210}\text{Pb}$ on the wind direction, although referred to a specific time interval, has been demonstrated in (6) as well as in (24). Indeed, the ratio of ${}^7\text{Be}/{}^{210}\text{Pb}$ activities increases when NW wind direction (from the sea) is prevalent, because the maritime air masses have a lower Radon concentration.

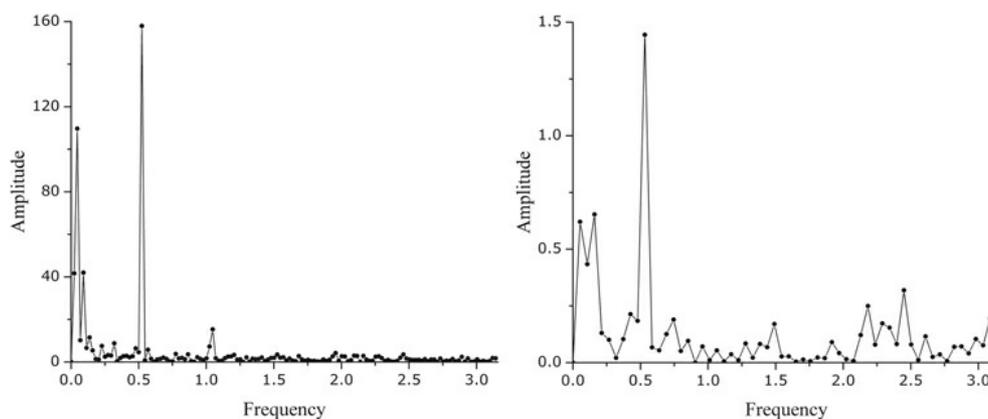
Figure 8. Monthly rainfall versus specific activities: Left: ${}^7\text{Be}$ and Right: ${}^{210}\text{Pb}$.



The specific activity time series have been reconstructed for the monthly and weekly average values in order to make homogeneous comparisons with available data from other geographical areas.

Statistical analyses of specific activity values and their ratios have been carried out by following methods reported in (11,15,19,26–29). In Figure 9, the results of the Fourier spectral analysis of the time series of monthly averages for the two radionuclides are shown. Both show a main peak corresponding to a 12-month period (the abscissa frequency value is in units of $2\pi/T$, with T in months). The ${}^7\text{Be}$ series also shows a secondary peak corresponding to a period of 11.5 years, close to the 11-year sunspot number cycle, and anti-correlated with it, as reported in (4). The same periodicity has been highlighted in the concentrations of heavy metals in sediments taken in the Gulf of Palermo (30).

Figure 9. Amplitude of the Fourier transform for the monthly average of the specific activities. Frequency units are $2\pi/T$, with T in months: left: ${}^7\text{Be}$ and right: ${}^{210}\text{Pb}$.



4. Conclusion

The correlations between the data series available for ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ in atmospheric particulate matter collected in Palermo in the period 1995–2005 have been studied. The frequency analysis has been carried out in order to highlight seasonal cycles. The statistical analysis shows a Gaussian distribution for ${}^7\text{Be}$ air concentrations whereas log-normal distributions characterize daily ${}^{210}\text{Pb}$ air concentration and ${}^7\text{Be}/{}^{210}\text{Pb}$ activity ratio. Frequency distributions of concentrations show a seasonal behavior, and an anti-correlation with the sunspot cycle is confirmed for ${}^7\text{Be}$. The analyses carried out show the importance of the processes of transport in the atmosphere and the influence of meteorological and climatic parameters in determining the concentrations in the air of the aforementioned radionuclides. Indeed, the annual frequency for both radionuclides and the almost constant activity ratio show that the variation in concentrations is more determined by movements of air masses rather than by their origin. This can be of help in all those activities where the study is foreseen with the use of tracers of the evolution of the air masses with the different weather and climate conditions and in relation to the different period of the year. The results of the study about the behavior of ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ air activity concentration and of ${}^7\text{Be}/{}^{210}\text{Pb}$ activity ratio confirm the suitability of the above-mentioned analyses as sensitive tools for studying air transport processes. The observed correlation between ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ concentrations

demonstrates that the air movement is more important than their origin to understand their behavior in the atmosphere.

Disclosure statement

No potential conflict of interest was reported by the authors.

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