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Measurements of ^{22}Na in the Atmosphere: Ground Level Activity Concentration Values from Wet and Dry Deposition Samples

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Abstract: Sodium-22 (^{22}Na, half-life 2.603 years) is a cosmogenic radionuclide mainly produced in the stratosphere by nuclear spallation reactions of cosmic rays on ^{40}Ar. Due to the very low concentration levels normally reached in the environment, ^{22}Na poses no significant radioprotection threats: actually, the effective doses delivered to humans can hardly exceed a few nSv per year, a very negligible value. However, the measurements of this radionuclides can be very interesting for atmospheric circulation and climatic studies. Unfortunately, the difficulty of ^{22}Na detection, due to its very low concentration levels, has prevented the gathering of large and widespread time series of this radionuclide. In this paper, a method for the retrospective measurements of ^{22}Na in the atmosphere, starting from the gamma spectra (hyperpure germanium detectors (HPGe) detectors) of wet and dry deposition samples stored in our databases is proposed and validated. The method was applied to spectra samples gathered in the context of the Italian National Radioactivity Monitoring Network (RESORAD) and allowed the detection of the very low atmospheric activity concentration values of ^{22}Na present at ground level. The results obtained with the new method are discussed and compared for validation with the available experimental values. Finally, some possible applications to environmental studies are also highlighted and suggested.

Keywords: ^{22}Na; atmospheric activity concentration; HPGe gamma spectra; retrospective analysis

1. Introduction

Sodium-22 (^{22}Na) is a β^+ cosmogenic radionuclide with a relatively long half-file (2.603 years), continuously produced by nuclear spallation reactions of cosmic rays on argon-40 (^{40}Ar) nuclei [1]. It decays into the stable isotope ^{22}Ne by β+ emission (90.35%) and electron capture (EC, 9.65%). Its production mainly occurs in the stratosphere and is essentially due to the high energy particles (E > 100 MeV/n) belonging to the galactic cosmic rays component (GCR, galactic cosmic rays). Once produced, ^{22}Na is quickly attached to the sub-micron particulate suspended in the atmosphere and slowly settles to the ground [2]. It is efficiently scavenged by precipitation, and therefore can also be found in meteoric waters, thereby easily entering into the ecosystems. Its concentrations in atmosphere increased substantially during the sixties of the 20th century, in the early phase of Cold War (1945–1963), due to nuclear weapons testing. At that time, traces of ^{22}Na were also measured in lichens, mosses and wild game [3,4]. Nowadays, since the last atmospheric nuclear weapon detonation occurred in 1980 (Lop Nor, China), the ^{22}Na levels returned to the typical pre-Cold War values: atmospheric concentrations usually well below 1 µBq/m^3 at ground level [5]. However, the main interest in studying

this radionuclide is its use as a tracer of the atmospheric circulation, often investigated also by means of other cosmogenic radionuclides with very different half-lives (for instance: [7]Be, $t_{1/2}$ = 53.22 days and [10]Be, $t_{1/2}$ = 1.36·10[6] years) [1]. A sudden increase of the ground level concentrations of the cosmogenic radionuclides, for example, can be used as indicator of the intrusion of air masses of stratospheric origin [6–9]. In this respect, the study of the ratio [22]Na/[7]Be could give very interesting information, as was recently pointed out in a recent study (Hoffmann, 2018, [10]).

Moreover, because the cosmogenic radionuclides' production rate is affected by the 11 year sun cycles, the activity concentration values of all cosmogenic radionuclides are also of great interest for monitoring solar activity [11–14]: [22]Na is particularly interesting in this respect, because of its physical characteristics, as its quite long half-life, make it less sensitive to variations of the meteorological conditions. Therefore, the availability of reliable time series of this radionuclide is very important and of great scientific relevance, allowing the gathering of some very interesting information that cannot be obtained using only easier-to-measure radionuclides, for example, [7]Be, usually present in larger concentrations.

2. Materials and Methods

In principle, [22]Na can be easily measured by γ spectrometry with hyperpure germanium detectors (HPGe): actually it emits a strong γ line at 1274.5 keV with a yield close to unity (99.94%) in a region of the spectrum only slightly influenced by the Compton background of the [40]K high energy γ emission (1460 keV). There is also another emission at 511 keV with an even stronger yield (180%) but not useful for quantitative determination due to the interference of the 511 keV γ annihilation peak always present in the background because of the pair production (electron e^- and positron e^+) interactions of γ radiation with matter, mainly due to the lead shielding. Unfortunately, in spite of its strong emissions, the very low concentration levels typically found in the atmosphere ($<$1 μBq/m^{3}) make the detection of [22]Na in normal atmospheric particulate samples often very difficult. For that reason, a huge amount of air (tens of thousands of cubic meters, at least) needs to be filtered in order to achieve the necessary sensitivity. Alternatively, an indirect measurement of the atmospheric activity concentrations can be done using deposition data. In fact, wet and dry deposition can be collected for a convenient sampling time τ (in our case, 1 month) by means of stainless steel tanks or similar containers. The relationship between the deposition values D (Bq/m^{2}) and their corresponding atmospheric activity concentrations C (Bq/m^{3}) can be deduced from a simple model describing the deposition D of radionuclides in a collection tank by the following differential Equation:

$$\frac{dD}{dt} + \lambda \times D = \Phi \tag{1}$$

where λ is the decay constant of the radionuclide and Φ is the corresponding downward flux, usually expressed as Bq/(m[2]·s). If the flux is assumed to be constant in time, the analytical solution of the above equation is straightforward and the amount of radioactivity collected in the tank during a generic sampling time τ is thus given by the following expression:

$$D = \frac{\Phi}{\lambda} \times \left(1 - e^{-\lambda \times \tau}\right) \tag{2}$$

The main limitation of this description is considering the [22]Na flux as a constant: an apparently crude approximation, very far from real conditions, being the deposition mainly governed by precipitations—a typical example of a discrete and non-regular phenomenon. Bulk deposition should be more precisely described as a two components process, as follows: $\Phi_{bulk} = \Phi_{dry} + \Phi_{wet}$, where for the dry component a very simple relationship holds: $\Phi_{dry} = C \times v_d$, in which C is the activity concentration, while v_d is the average value of the settling velocity of the atmospheric particulate. A much more complicated expression should be used for the wet deposition component instead, involving many experimental parameters, such as the amount and the intensity of the precipitation

event, the height of the atmospheric column scavenged by the rain, the scavenging coefficients, etc. However, in real cases, the simultaneous knowledge of all these parameters is seldom available, thereby preventing the possibility of using a "true" theoretical wet deposition mathematical model. Fothat reason, a very simplified description is often proposed, with bulk deposition modelled using the same relationship that holds for dry deposition:

$$\Phi_{\text{bulk}} = C \times v_m \tag{3}$$

in which C is still the activity concentration, while v_m is a mean deposition velocity experimentally evaluated after measuring simultaneously the deposition data (see Equation (2) and the corresponding activity concentration C in atmosphere [15,16]. In doing so we must bear in mind that the physical meaning of v_m is quite different respect to that of v_d: while v_d is a mean velocity obtained averaging over the distribution of all the velocities of the settling particulate suspended in atmosphere, v_m is not a real velocity, just an empirical parameter encompassing the effect of dry deposition and precipitation, and whose dimensions are those of a velocity. For that reason the numerical values of v_m are much greater that those of v_d, the latter being related only to the much slower dry deposition processes: experimental measurements performed on ^{137}Cs gave for v_m a value around 0.04 m/s [16], while typical values of v_d, strongly dependent on the particulate diameter and other factors as well [17], are typically in the range 0.1–0.001 cm/s.

The experimental set up for the collection of the wet and dry deposition samples is a stainless steel tank placed on the roof of the laboratory building (see Figure 1). The bottom of the tank is always kept wet in order to prevent resuspension during dry periods. The collection of the samples is done at the end of each month: the tank is emptied and carefully washed with distilled water. The resulting water is then reduced by evaporation (90 °C) and brought to dryness. The residue is finally weighted, put in a little cylindrical jar (see Figure 2) and counted with hyperpure germanium detectors (HPGe) for 16 h.

Figure 1. The stainless steel tank for sampling wet and dry deposition on the roof of the ARPA Piemonte building (Via Jervis, 30, Ivrea, 10015, Italy): the collection area is about 4 m^2 wide. The tank is emptied on a monthly basis through a tube.

Figure 2. Plastic jar for the wet and dry deposition measurements placed on the top of the cap of a hyperpure germanium detectors (HPGe) detector. The dry residue (about 4 g) is uniformly distributed in a thin cylindrical shaped geometry.

These are the standard procedures followed in the context of the Italian Environmental Radioactivity National Monitoring Network (RESORAD): they allow reaching a quite-good sensitivity for most radionuclides. For instance, the MDA (minimum detectable activity), referred to as ^{137}Cs, was about 0.015 Bq/m^2, while for ^{22}Na a slightly larger value applies, 0.025 Bq/m^2, due to a lower spectrometric efficiency at the high energy γ emission of sodium-22 (1274.5 keV). It can be demonstrated that these deposition MDA values correspond to about 0.2–0.3 μBq/m^3 for the activity concentration: very low values are perfectly adequate for monitoring purposes, but still not enough for a continuous monitoring of ^{22}Na in atmosphere, as at ground level the ^{22}Na activity concentrations are sometimes even lower [5].

Therefore, in order to improve the sensitivity of the measurements, single annual samples were assembled, simply mixing the 12 monthly samples: each monthly sample of a given year (4 g of dry residue) was transferred into a larger jar (Figure 3) and counted as a new composite annual sample.

Operating in this way, a significant decrease of the MDA values for deposition is expected, as can be easily calculated using the simple, classic MDA formula given by Currie in 1968 [18]:

$$MDA_D = \frac{4.66 \times \rho_{back}}{\varepsilon_\gamma \times r_\gamma \times S \times \sqrt{t}} \tag{4}$$

where t is the counting time, ρ_{back} is the standard deviation of the background, ε_γ is the photopeak efficiency of the HPGe detector at the specific radionuclide emission energy, r_γ is the γ yield of the emission and S is the surface area. From this expression, taking into account Equations (2) and (3), the expression for the MDA activity concentrations can be written as follows:

$$MDA_C = \frac{4.66 \times \rho_{back} \times \lambda}{\varepsilon_\gamma \times r_\gamma \times S \times \sqrt{t} \times (1 - e^{-\lambda\tau}) \times v_m} \tag{5}$$

in which the sampling time τ is 1 month for the standard samples and 1 year for the composite sample. The improvement of the MDA values for annual measurements is due to the increased value of the quantity *(1−e^{−λτ})*, a factor that largely dominates two negative effects: (1) the decrease of the photopeak efficiency ε_γ caused by increasing of the solid angle of the counting geometry; (2) the slight increase of the Compton background standard deviation related to the greater sizof the annual sample. In order to boost further the sensitivity performances of the γ spectrometry, the counting times were also increased from the standard value (57,600 s) up to 200,000 s. In Table 1 all the factors contributing to the variation of the MDA values are summarized, with monthly measurements taken as reference.
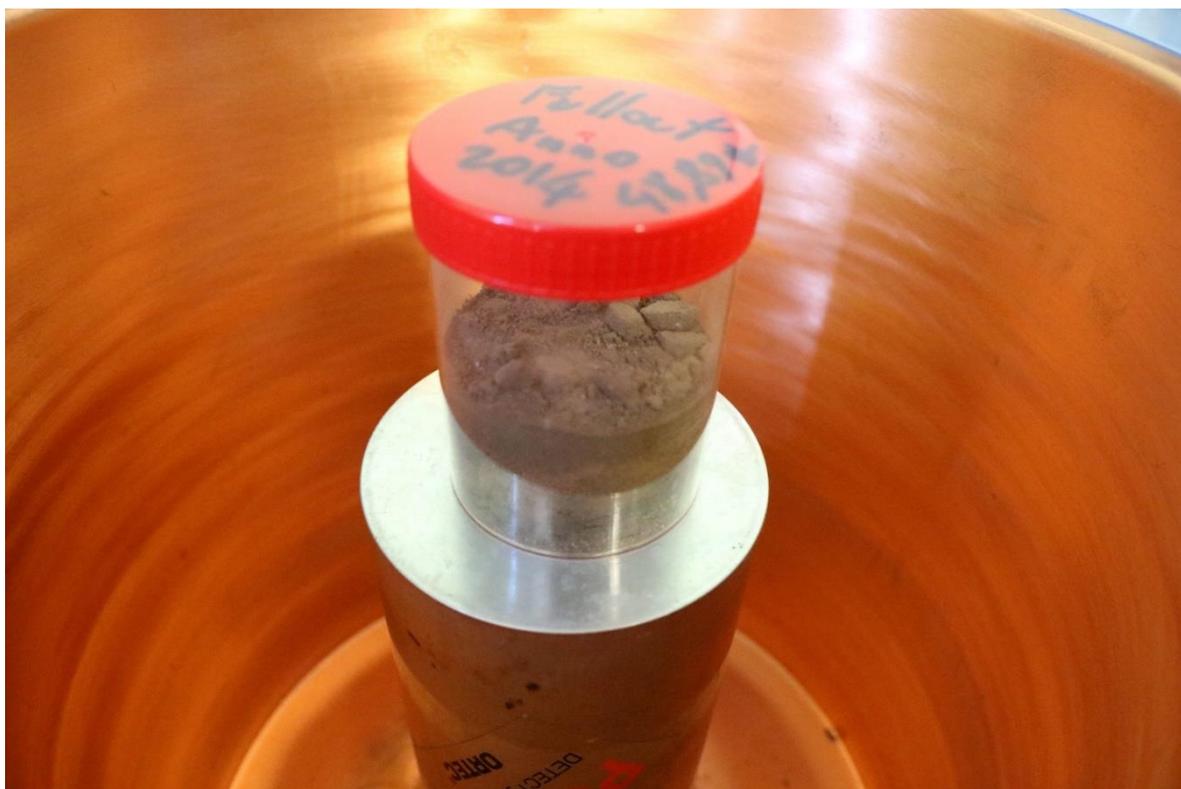

Figure 3. Jar containing an annual sample, made up putting together and mixing 12 monthly samples, ready to be counted on the top of the cap of a HPGe γ detector.

Table 1. Multiplying factors affecting MDA values: monthly measurements taken as reference.

Sampling Time	*(1−e^{−λτ})*	ε_γ @ 1274.5 keV	ρ_{back}	Counting Time	Overall Factor
Monthly measurement	1	1	1	1	1
Annual measurement	0.0947	1.586	1.889	0.537	0.152

Operating in this way we were able to considerably lower the MDA values down to $MDA_C \approx 0.05$ µBq/m^3, at least a factor of 5–6 better than the previous typical values: MDA_C levels of this order of magnitude are supposed to be adequate for the detection of the very low ground level ^{22}Na activity concentrations.

Thus, the 12 monthly samples collected from 2014 to 2018 (five years) were put together, mixed and counted as five annual composite samples. Unfortunately, this approach could not be extended to samples older than 6–7 years, because the residual radioactivity present in the samples reaches undetectable levels due to the relatively short half-life of ^{22}Na (2.603 years). Therefore, to work

around the problem, we followed a method recently proposed in [19]. The method, called the spectral summation technique, is based on the very simple idea to build a virtual, annual spectrum simply by summing channel by channel, the γ rays counts recorded in each monthly spectrum: of course, the new virtual spectrum will not be affected by the ^{22}Na decay issue, as each monthly spectrum was previously acquired shortly after the collection of the samples. The virtual reconstructed annual spectrum will be equivalent to an annual spectrum of the same size acquired with a much longer counting time (twelve times the typical counting time of a monthly spectrum), thereby resulting in a substantial reduction of the MDA value.

In order to avoid distortion phenomena, the summation operations should be performed with great care: only the spectra acquired with the same spectrometer and with the same channel-energy calibration data can be summed: even small calibration differences and slight shifts can shatter the final result, reducing the detection capabilities.

The typical sensitivity performance of the virtual spectrum can be estimated by means of Equation (5), inserting the proper values of all the relevant parameters. We have found thusly that $\text{MDA}_C \approx 0.07 \; \mu\text{Bq/m}^3$, a value very close to the experimental one, obtained with the composite sample (Figure 3).

3. Results and Discussion

In Figures 4 and 5 the measured γ spectra of the annual samples 2018 and 2014 are shown. Both spectra look very similar: the 1274.5 keV ^{22}Na emission, marked in red, is always present, while in the 2014 spectrum the peak is considerably smaller. The only relevant difference is the lack of the 477.6 keV ^{7}Be peak in the 2014 spectrum, because it completely disappeared due to decay.
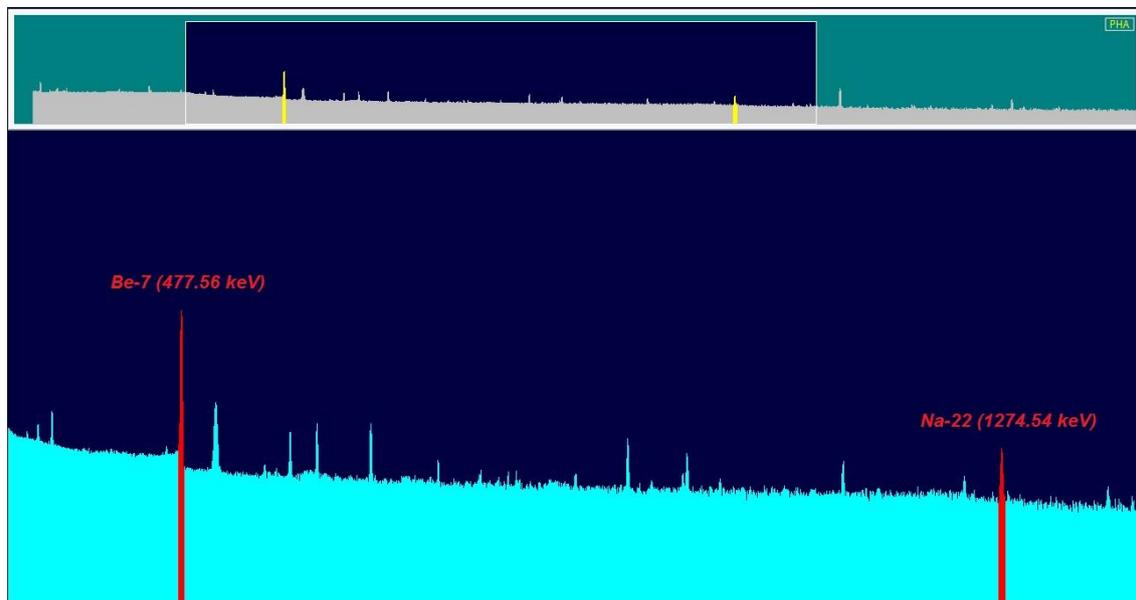

Figure 4. The annual spectrum of 2018: The ^{22}Na peak marked in red is evident in the higher energy part of the spectrum. The other marked peak belongs to ^{7}Be, the most abundant cosmogenic radionuclide in atmosphere.
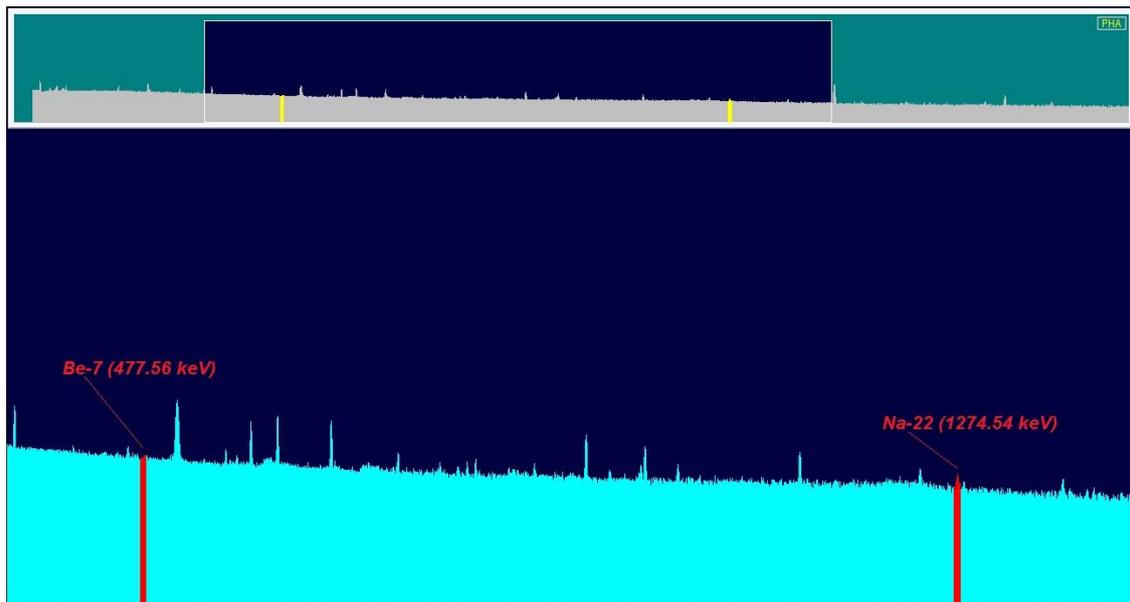
Figure 5. The annual spectrum of 2014: The ^{22}Na peak is still evident, but much smaller with respect to that in Figure 4. Moreover, the ^{7}Be peak completely disappeared due to decay.

In Figures 6 and 7, the corresponding 2018 and 2014 annual spectra, reconstructed from the recorded monthly γ spectra by means of the spectral summation, are shown.
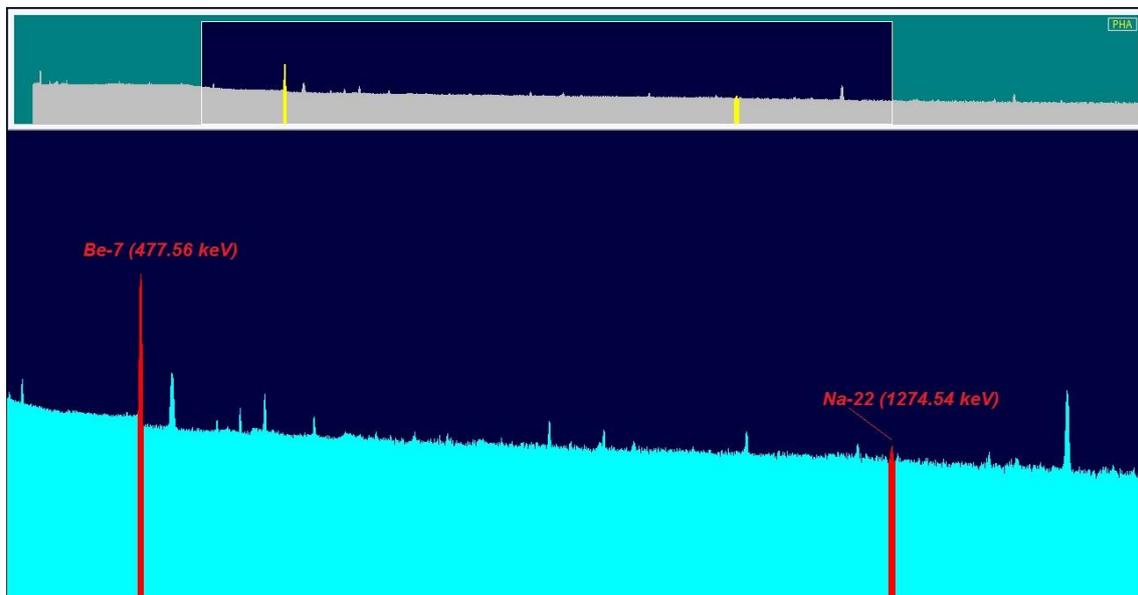

Figure 6. Annual summation spectrum for 2018: Both ^{22}Na and ^{7}Be peaks are present. The ^{22}Na peak in the composite spectrum is significantly smaller than that in the corresponding measured spectrum (Figure 4).
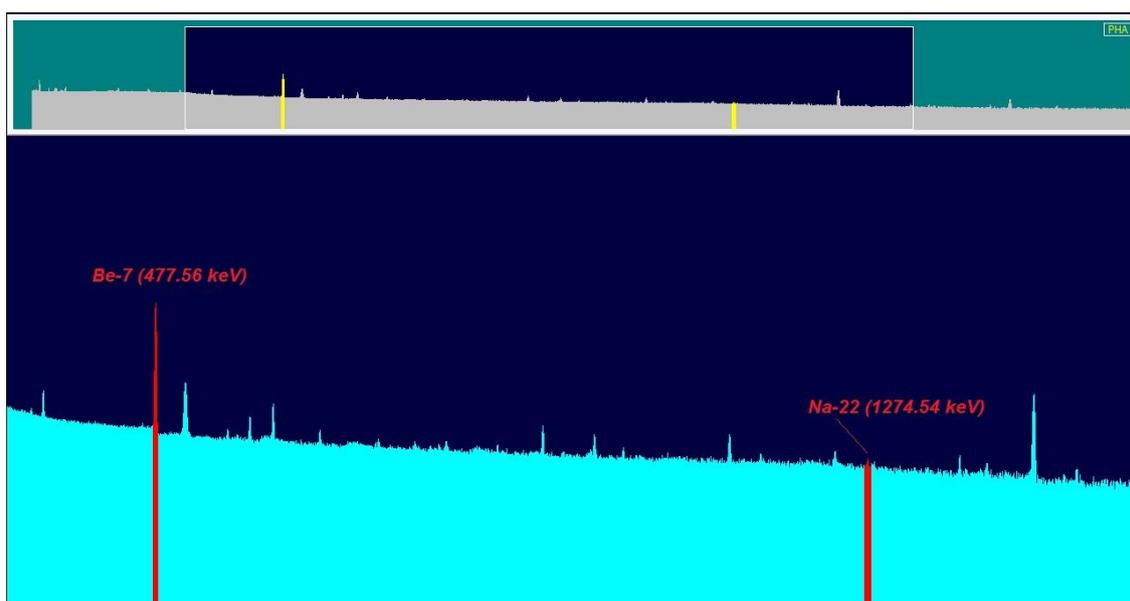
Figure 7. Annual summation spectrum for 2014: Both ^{22}Na and ^{7}Be peaks are present. It is worth noting that in the 2014 measured spectrum (see Figure 5) the ^{7}Be peak is missing.

The detection of the ^{22}Na peaks in the reconstructed spectra obtained with the spectrum summation technique is certainly a good achievement. However, in order to quantitively compare the results obtained with these two different approaches, an additional step is needed. Actually, the two deposition data sets, D_a and D_m, show values that differ from each other by about one order of magnitude, as shown in Table 2.

Table 2. ^{22}Na annual deposition values from 2014 to 2018.

Year	Measured D_a (Bq/m^2)	Reconstructed D_m (Bq/m^2)	Rain (mm)
2018	0.7604 ± 5.8%	0.0529 ± 10.1%	1520.9
2017	0.3977 ± 13.1%	0.1022 ± 12.0%	736.8
2016	0.5429 ± 9.6%	0.0207 ± 25.3%	1122.4
2015	0.5027 ± 9.2%	0.0268 ± 17.9%	866
2014	0.4800 ± 15.8%	0.0253 ± 18.1%	1655.4

In Table 2 the annual precipitation values (mm of rain) recorded at the sampling site (Ivrea) are reported as well, because it is a relevant parameter for deposition mechanisms.

The reason for these discrepancies can be explained taking into account that, for measured values, the measured deposition quantity, i.e., the annual deposition D_a, is given by the expression:

$$D_a = \frac{\Phi}{\lambda} \times \left(1 - e^{-\lambda \times \tau a}\right) \tag{6}$$

where Φ is the downward flux of the radionuclide (Bq/(m^2·s) and τ_a = 1 year is the sampling time, while for the reconstructed deposition D_m the following holds:

$$D_m = \frac{\Phi}{\lambda} \times \left(1 - e^{-\lambda \times \tau m}\right) \tag{7}$$

in which τ_m = 1 month. being monthly collected deposition. The downward flux Φ can thus be evaluated independently using the two different Equations (6) and (7), using as a normalization factor the proper $(1-e^{-\lambda\tau})$ quantity. One can argue that the comparison between the two methods should be made, more significantly, in terms of the activity concentrations C instead of the fluxes Φ. This is very

easy to do: Taking into account Equation (3) the following equation (Equation (8)) can be obtained, allowing a direct calculation of the atmospheric activity concentration values fromhe deposition data:

$$C = \frac{D \cdot \lambda}{(1 - e^{-\lambda \tau}) \times v_m} \tag{8}$$

in which for all data the average value v_m = 0.04 m/s were used [16]. The activity concentration values calculated with Equation (8) are then plotted for comparison in Figure 8. The overall uncertainty of C is largely dominated by the v_m component and can be estimated of the order of 20%.

(a)

(b)
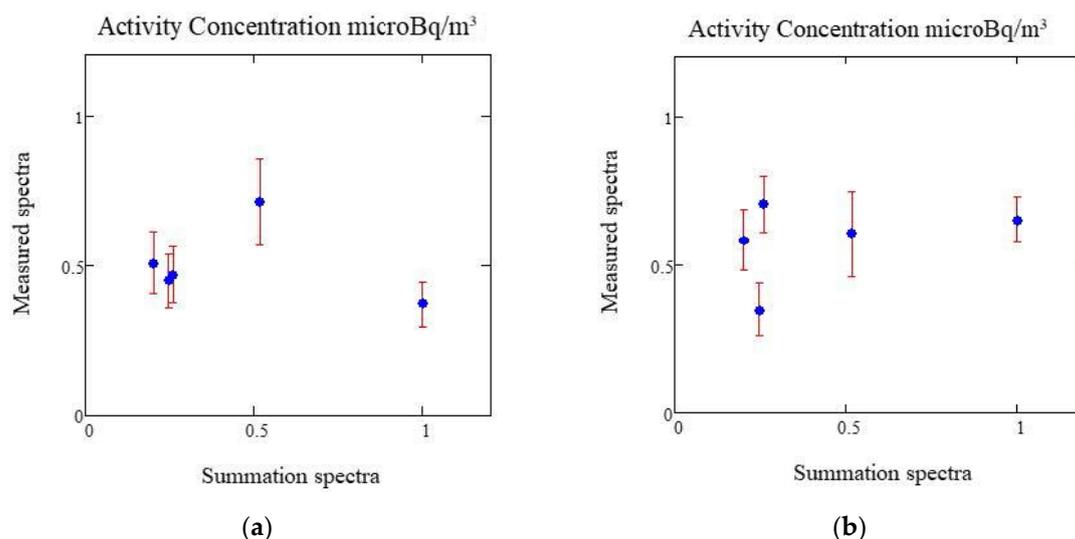
Figure 8. Comparison of the [22]Na activity concentration values measured and obtained with the spectral summation technique: in the first panel (**a**) are displayed the raw data while in (**b**) the rain normalized ones.

In the panel a, the raw data are displayed: at first sight no apparent linear trend appears, while the removal of the data with the highest summation spectral value (year 2017; C ≈ 1 µBq/m^3) would lead to a quite good linear correlation (R^2 = 0.871). The exclusion of this data could be supported by the consideration that particularly low rainfall values occurred in 2017 (see Table 2): actually, it has already pointed out that the overall amount of precipitation can substantially affect the "real" v_m value, a parameter that plays an essential role in the calculation of the activity concentration C. Therefore, a different approach can be tried, normalizing all the activity concentration data to the average precipitation rate in the period 2014–2018, as follows: $C_{n_i} = C_i \cdot \frac{P_m}{P_i}$, where C_{n_i} are the normalized values, P_m is the average precipitation value in that period and the subscript i refers to each individual activity concentration value. The normalized results are shown in the panel b: while some discrepancies still remain, the correlation seems improved. The agreement of the two data sets could probably be improved further with a more precise and sophisticated normalization procedure, taking into account not only the overall precipitation values but also the number of precipitation events and their distribution along the year. Nevertheless, in spite of these still open issues, the obtained results show that the spectral summation technique applied to the deposition data are able to detect the low level [22]Na traces in the atmosphere, giving values that in most cases are in fairly good agreement (within 25%–30%) with the measured ones.

The reconstruction of long time series of this (and maybe others) radionuclide from old stored spectra is therefore a realistic perspective, very promising for several environmental studies.

However, as an example, some preliminary interesting results can be shown. Taking as the most reliable estimation for the [22]Na annual activity concentrations, the average of the measured and reconstructed values, and plotting them versus time, an apparent increasing trend appears (Figure 9).
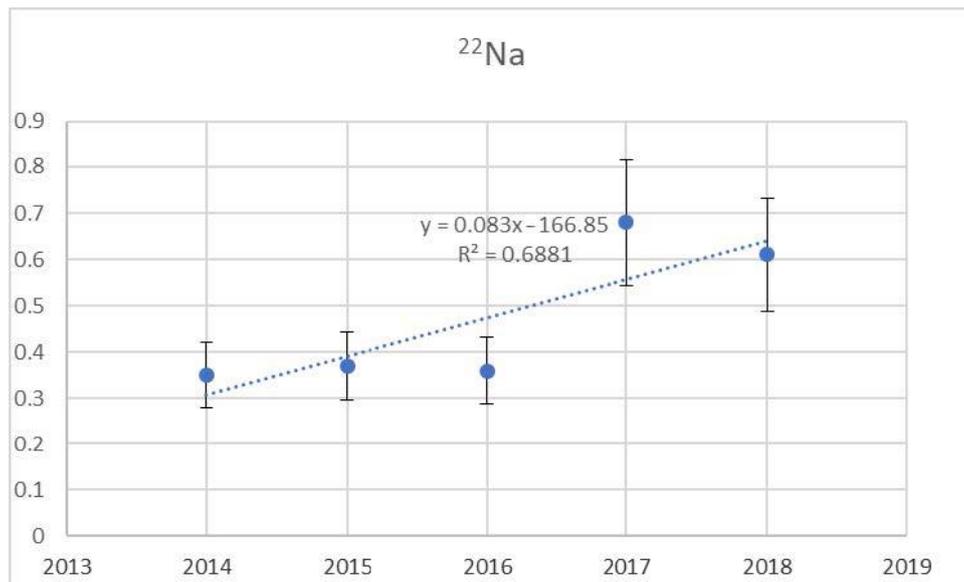
Figure 9. In the last few years the ^{22}Na activity concentration values show an apparently increasingly trend.

This trend is consistent with the corresponding decrease of solar activity that we experienced in those years due to the well-known 11 year solar cycle (in particular, the end of the 24th solar cycle), leading to an increase of the GCR component, and thus to greater production rates of all cosmogenic radionuclides.

In Figure 10 the ^{22}Na activity concentrations data available at the moment are plotted together with the periodically varying, yearly averaged sunspot numbers, taken as a proxy for solar activity [20–22]: as expected, the data clearly seem to be inversely correlated with the average sunspot numbers. The calculation by means of the summation spectra technique of the ^{22}Na activity concentration in the past few years until the beginning of this century is currently on the way and will allow us to verify these conclusions in a broader time range.
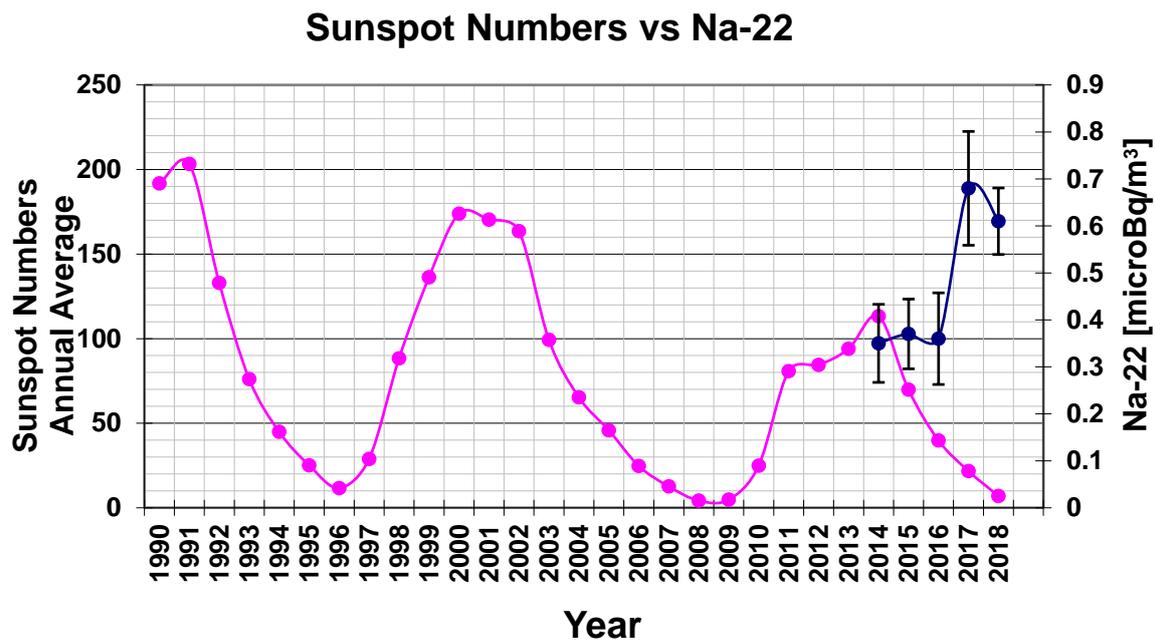

Figure 10. Sunspot numbers (magenta) and ^{22}Na (blue) ground level atmospheric activity concentrations displayed with their uncertainty bars.

References

1. LNE-LNHB/CEA Table de Radionucléides. Available online: www.nucleide.org/DDEP_WG/Nuclides (accessed on 30 September 2019).

2. Lal, D.; Peters, B. Cosmic ray produced radioactivity on the Earth. In *Handbuch der Physik*; Springer: Berlin, Germany, 1967; Volume 46/2, pp. 552–616.

3. Magnoni, M. Chapter 12—Environmental Radioactivity and Radioecology. In *Physical Agents in the Environment and Workplaces-Noise and Vibrations, Electromagnetic Fields and Ionizing Radiation*; Licitra, G., d'Amore, G., Magnoni, M., Eds.; Taylor and Francis Group; LLC: Boca Raton, USA, 2018.

4. NCRP. *Report n° 94, Exposure of the Population in the United States and Canada from Natural Background Radiation*; NCRP: Bethesda, MD, USA, 1987.

5. Blazej, S.; Mietelski, J.W. Cosmogenic Na-22, Be-7 and terrestrial Cs-137, K-40 radionuclides in ground level air samples collected in Krakow (Poland) over years 2003–2006. *J. Radioanal. Nucl. Chem.* **2014**, *300*, 747–756. [CrossRef] [PubMed]

6. Dutkiewicz, V.A.; Husain, L. Stratospheric and tropospheric components of 7Be surface air. *J. Geophys. Res.* **1985**, *90*, 5783–5788. [CrossRef]

7. Dutkiewicz, V.A.; Husain, L. Determination of stratospheric ozone at ground level using ^{7}Be/ozone ratios. *Geophys. Res. Lett.* **1979**, *6*, 171–174. [CrossRef]

8. Vieeze, W.; Singh, H.B. The distribution of beryllium-7 in the troposphere: Implication on stratospheric-tropospheric exchange. *Geophys. Res. Lett.* **1980**, *7*, 805–808. [CrossRef]

9. Yoshimori, M. Production and behaviour of beryllium-7 isotope in the upper atmosphere. *Adv. Space Res.* **2005**, *36*, 922–926. [CrossRef]

10. Hoffman, I.; Lewis, B.; Chan, P. Circulation of cosmogenic ^{22}Na using the global monitoring network o the Comprehensive Nuclear-Test-Ban-Treaty Organization (CTBTO). *J. Environ. Radioact.* **2018**, *187*, 8–15. [CrossRef] [PubMed]

11. European Radiation Dosimetry Group. *Radiation Protection 85, Exposure of Air Crew to Cosmic Radiation*; EURADOS report 1996-01; European Radiation Dosimetry Group: EC, Brussels, Belgium and Luxemburg, Luxemburg, 1996.

12. O'Brien, K.H. Secular variation in the production of cosmogenic isotopes in earth's atmosphere. *J. Geophys. Res.* **1979**, *84*, 423–431. [CrossRef]

13. Damatto, S.R. Be-7 measured at ground air level and rainfall in the city of Sao Paulo. In Proceedings of the INAC 2013—International Nuclear Atlantic Conference, Recife, Brazil, 24–29 November 2013; ISBN 978-85-99141-05-2.

14. Field, C.V.; Schmidt, G.A.; Koch, D.; Salyk, C. Modeling production and climate related impacts of ^{10}Be concentrations in ice cores. *J. Geophys. Res.* **2006**, *111*, D15107. [CrossRef]

15. Magnoni, M. La deposizione umida e secca: Aspetti sperimentali e teorici. In Proceedings of the Congress 'Twenty-Five Years After Chernobyl Accident: Studies, Remarks and Recent Findings', Udine, Italy, 10–12 March 2011.

16. Facchinelli, A.; Magnoni, M.; Gallini, L.; Bonifacio, E. 137Cs contamination from Chernobyl of soils in Piemonte (North-West Italy): Spatial distribution and deposition model. *Water Air Soil Pollut.* **2002**, *134*, 341–352. [CrossRef]

17. Giardina, M.; Buffa, P. A new approach for modeling dry deposition velocity of particles. *Atmos. Environ.* **2018**, *180*, 11–22. [CrossRef]

18. Currie, L.A. Limit of Qualitative Detection and Quantitative Determination. *Anal. Chem.* **1968**, *40*, 586–593. [CrossRef]

19. Hoffman, I.; Lewis, B.; Chan, P.; Ungar, K. Hoffman Analysis of ^{22}Na using a spectral summation technique on high-volume aerosol samples. *J. Environ. Radioact.* **2017**, *169*, 151–158. [CrossRef] [PubMed]

20. SILSO, Royal Observatory of Belgium. Available online: www.sidc.be/SILSO (accessed on 14 November 2019).

21. Hoyt, D.V.; Schatten, K.H. Group sunspot numbers: A new solar activity reconstruction. Part 1. *Sol. Phys.* **1998**, *179*, 189–219. [CrossRef]

22. Hoyt, D.V.; Schatten, K.H. Group sunspot numbers: A new solar activity reconstruction. Part 2. *Sol. Phys.* **1998**, *181*, 491–512. [CrossRef]