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

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Abstract: Sodium-22 ($^{22}\text{Na}$, half-life 2.603 years) is a cosmogenic radionuclide mainly produced in the stratosphere by nuclear spallation reactions of cosmic rays on $^{40}\text{Ar}$. Due to the very low concentration levels normally reached in the environment, $^{22}\text{Na}$ 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 radionuclide can be very interesting for atmospheric circulation and climatic studies. Unfortunately, the difficulty of $^{22}\text{Na}$ 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 $^{22}\text{Na}$ 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 $^{22}\text{Na}$ 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: $^{22}\text{Na}$; atmospheric activity concentration; HPGe gamma spectra; retrospective analysis

1. Introduction

Sodium-22 ($^{22}\text{Na}$) is a $\beta^+ $ cosmogenic radionuclide with a relatively long half-file (2.603 years), continuously produced by nuclear spallation reactions of cosmic rays on argon-40 ($^{40}\text{Ar}$) nuclei [1]. It decays into the stable isotope $^{22}\text{Ne}$ by $\beta^+ $ 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, $^{22}\text{Na}$ 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 $^{22}\text{Na}$ 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 $^{22}\text{Na}$ levels returned to the typical pre-Cold War values: atmospheric concentrations usually well below 1 $\mu$Bq/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, $t_{1/2} = 1.36 \times 10^6$ 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 $\gamma$ spectrometry with hyperpure germanium detectors (HPGe): actually it emits a strong $\gamma$ 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 $\gamma$ 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 $\gamma$ annihilation peak always present in the background because of the pair production (electron $e^-$ and positron $e^+$) interactions of $\gamma$ 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 ($<1 \mu$Bq/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 $\tau$ (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:

$$\frac{dD}{dt} + \lambda \times D = \Phi$$  \hfill (1)

where $\lambda$ is the decay constant of the radionuclide and $\Phi$ 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 $\tau$ is thus given by the following expression:

$$D = \frac{\Phi}{\lambda} \times \left(1 - e^{-\lambda \times \tau}\right)$$  \hfill (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: $\Phi_{\text{bulk}} = \Phi_{\text{dry}} + \Phi_{\text{wet}}$, where for the dry component a very simple relationship holds: $\Phi_{\text{dry}} = C \times \bar{v}_d$, in which $C$ is the activity concentration, while $\bar{v}_d$ 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. For that reason, a very simplified description is often proposed, with bulk deposition modelled using the same relationship that holds for dry deposition:

\[ \Phi_{\text{bulk}} = C \times v_m \]  

(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 than those of \( v_d \), strongly dependent on the particulate diameter and other factors as well [17], and 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 m² wide. The tank is emptied on a monthly basis through a tube.
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 $^{137}\text{Cs}$, was about 0.015 Bq/m$^2$, while for $^{22}\text{Na}$ a slightly larger value applies, 0.025 Bq/m$^2$, due to a lower spectrometric efficiency at the high energy $\gamma$ emission of sodium-22 (1274.5 keV). It can be demonstrated that these deposition MDA values correspond to about 0.2–0.3 $\mu$Bq/m$^3$ for the activity concentration: very low values are perfectly adequate for monitoring purposes, but still not enough for a continuous monitoring of $^{22}\text{Na}$ in atmosphere, as at ground level the $^{22}\text{Na}$ 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]:

$$ MDA_D = \frac{4.66 \times \rho_{\text{back}}}{\epsilon_{\gamma} \times r_{\gamma} \times S \times \sqrt{t}} $$

(4)

where $t$ is the counting time, $\rho_{\text{back}}$ is the standard deviation of the background, $\epsilon_{\gamma}$ is the photopeak efficiency of the HPGe detector at the specific radionuclide emission energy, $r_{\gamma}$ is the $\gamma$ 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:

$$ MDA_C = \frac{4.66 \times \rho_{\text{back}} \times \lambda}{\epsilon_{\gamma} \times r_{\gamma} \times S \times \sqrt{t} \times (1 - e^{-\lambda t}) \times \nu_m} $$

(5)
in which the sampling time $\tau$ 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 $(1-e^{-\lambda\tau})$, a factor that largely dominates two negative effects: (1) the decrease of the photopeak efficiency $\epsilon_\gamma$, 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 size of the annual sample. In order to boost further the sensitivity performances of the $\gamma$ 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](image-url) 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 $\gamma$ detector.

| Sampling Time       | $(1-e^{-\lambda\tau})$ | $\epsilon_\gamma$ @ 1274.5 keV | $\rho_{\text{back}}$ | Counting Time | Overall Factor |
|---------------------|-------------------------|----------------------------------|-----------------------|----------------|----------------|
| Monthly measurement | 1                       | 1                                | 1                     | 1              | 0.152          |
| Annual measurement  | 0.0947                  | 1.586                            | 1.889                 | 0.537          | 1              |

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

Operating in this way we were able to considerably lower the MDA values down to $\text{MDA}_C \approx 0.05 \, \mu\text{Bq/m}^3$, at least a factor of 5–6 better than the previous typical values: $\text{MDA}_C$ levels of this order of magnitude are supposed to be adequate for the detection of the very low ground level $^{22}\text{Na}$ 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 $^{22}\text{Na}$ (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 22Na 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 22Na 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 7Be peak in the 2014 spectrum, because it completely disappeared due to decay.

![Figure 4](image-url)

**Figure 4.** The annual spectrum of 2018: The 22Na peak marked in red is evident in the higher energy part of the spectrum. The other marked peak belongs to 7Be, 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 $\gamma$ 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).
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 quantitatively 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/m²) | Reconstructed $D_m$ (Bq/m²) | 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%          | 0.0266 ± 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:

$$ D_a = \frac{\Phi}{\lambda} \times \left(1 - e^{-\lambda \times \tau_a}\right) $$

where $\Phi$ is the downward flux of the radionuclide (Bq/(m²-s)) and $\tau_a = 1$ year is the sampling time, while for the reconstructed deposition $D_m$ the following holds:

$$ D_m = \frac{\Phi}{\lambda} \times \left(1 - e^{-\lambda \times \tau_m}\right) $$

in which $\tau_m = 1$ month. Being monthly collected deposition. The downward flux $\Phi$ can thus be evaluated independently using the two different Equations (6) and (7), using as a normalization factor the proper $(1-e^{\lambda \tau_f})$ 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 $\Phi$. 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 from the deposition data:

\[ C = \frac{D \cdot \lambda}{(1 - e^{-\lambda t})} \times v_m \]  

in which for all data the average value \( v_m = 0.04 \text{ m/s} \) 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%.

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; \( C \approx 1 \text{ µBq/m}^3 \)) 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: \( C_{ni} = C_i \frac{P_m}{P_i} \), where \( C_{ni} \) 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 \( ^{22}\text{Na} \) 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 \( ^{22}\text{Na} \) annual activity concentrations, the average of the measured and reconstructed values, and plotting them versus time, an apparent increasing trend appears (Figure 9).
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.
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