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Analysis of ^{22}Na using a spectral summation technique on high-volume aerosol samples

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ABSTRACT

Measurement of cosmogenic ^{22}Na in daily aerosol samples is often difficult due to low atmospheric production rates. A new technique based upon spectral summation of sequential high-volume aerosol samples to measure ^{22}Na is described and validated. This summation technique has broad applications to any detection system that produces sequential representative sample measurements in which radioisotopes are just below the detection limit, provided the energy calibration is stable. It is anticipated that a global dataset of this radionuclide will have many important environmental science applications.

1. Introduction

Cosmogenic radionuclides are very useful in environmental studies, serving as tracers, tracking the path of pollutants and other materials in the environment and possibly the duration of transport or atmospheric residence time (Lal et al., 1958; Heikkilä et al., 2008, 2009; Igarashi et al., 1998; Koch and Rind, 1998; Raisbeck et al., 1981; Długosz-Lisiecka and Bem, 2012). Simultaneous measurements of two different cosmogenic radionuclides with significantly different half-lives ($t_{1/2}$), such as ^{7}Be ($t_{1/2}$ = 53.22d) and ^{10}Be ($t_{1/2}$=1.51×10^{6}a) can form a radiochronometer, where changes in the relative concentrations provide valuable timing information on environmental processes.

The challenge of using ^{10}Be as an environmental tracer is that due to the long half-life, it cannot be measured through a radioactive decay process. For measurement, an Accelerator Mass Spectrometer (AMS) is necessary. The relatively high cost and specialized nature of this equipment forms a significant barrier to its widespread use. For global environmental studies, such as those involving the bulk circulation of the atmosphere, an alternate tracer, ideally with a greater density of data, is desirable.

One candidate cosmogenic radionuclide is ^{22}Na. With an intermediate half-life ($t_{1/2}$=2.6027a) between that of ^{7}Be and ^{10}Be, ^{22}Na is ideal for many environmental studies on the occurrence of processes of up to several years. Although measurement of ^{22}Na does not require an AMS, quantification of cosmogenic ^{22}Na in daily aerosol samples is often difficult primarily due to low production rates that require extended aerosol sampling intervals. One problem with ^{22}Na is that data on this nuclide is scarce and confined to narrow time periods and locations (Długosz-Lisiecka and Bem, 2012; Jasiulionis and Wershofen, 2005; Leppänen et al., 2012; Steinmann et al., 2013; Luyanas et al., 1970; Fleishman, 2008; Błażej and Mietelski, 2014; Leppänen and Grinsted, 2008). A global inventory over a broad time period of ^{22}Na is currently absent in the literature and this study aims to fill this gap.

Although a small amount of production occurs in the troposphere, the majority (67%) occurs in the stratosphere through the spallation of cosmic rays on ^{40}Ar (Kulan et al., 2006a, 2006b). The low concentration of ^{40}Ar and the generally well isolated stratosphere make ground-level observations extremely rare (Beer and McCrackenvon Steiger Rudolf, 2012). Observations are therefore restricted to sites with very specific atmospheric circumstances (Jasiulionis and Wershofen, 2005). The typical ground-level observation scenario occurs when strong vertical down-mixing occurs in the atmosphere, which carries stratospheric ^{22}Na directly to the air sampler (Leppänen and Grinsted, 2008).

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A different technique, spectral summation, was performed to more consistently quantify ^{22}Na in aerosol samplers before performing a gamma spectroscopy analysis. The results of this analysis will create the first global dataset of ^{22}Na activity concentration values. This dataset is envisioned to be useful for at least two principal applications. First, a large global set of environmental radioactivity measurements can be used in environmental studies through its use as a atmospheric or hydrological tracer. For example, data from this study could be used to improve the accuracy of bulk air circulation models or study specific atmospheric phenomena such as Stratosphere-Troposphere Exchange (STE). Second, this technique may provide a means to obtain additional information on individual samples of interest. More specifically, it may be possible to infer the "history" of an airmass by looking at ratios of ^{22}Na and ^{7}Be. By examining the relative ^{22}Na and ^{7}Be concentrations, the relative time spent in the stratosphere and troposphere by the airmass could be better understood. For example, if the concentration of ^{22}Na increases relative to ^{7}Be, it indicates the stratospheric air (younger) has mixed more efficiently with the tropospheric (older) air.

2. Material

The primary data source is the aerosol subnetwork of the International Monitoring System (IMS), a multi-technology network comprised of acoustic and radiological monitoring sites that support the verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT), which bans nuclear explosions in all environments. The aerosol monitoring sites were designed to detect nuclear explosions by sampling radioactive debris from the atmosphere. In addition to the verification mission, the high volume (typically $>20{,}000 m^3 d^{-1}$) samples collected at each site in this network are also ideal for environmental studies. The location of the aerosol monitoring sites of the CTBT are shown in Fig. 1 while the station codes and monitoring site locations are given in Table 1.

Although there is a mix of fully automatic and manual aerosol sampling (in terms of filter changing) in the network, at every monitoring site is a dedicated High-Purity Germanium (HPGe) detector. This design essentially makes these systems very similar to an environmental radioactivity laboratory, even though many sites are located in remote locations. The sampling and analysis system operates with a 24 h sampling period, followed by a 24 h delay to let the radon and other short-lived progeny decay before a 24 h spectral acquisition period. The radioactive decay that would occur during transport from sample collection to laboratory analysis is not a factor in the IMS, as all samples have their spectral acquisition performed onsite. This retains measurement sensitivity where transport time can be a significant proportion of a half-life for some short-lived analytes, such as ^{7}Be. One of the principal reasons this network is a good choice for the summation technique is that the detection systems are designed to be highly stable due to the remote and often harsh environments present at many of the installation sites.

One major problem with measuring ^{22}Na is that almost every daily aerosol sample collected has insufficient ^{22}Na activity for reliable detection. For the CTBT IMS air samplers, typical ^{7}Be Minimum Detectable Concentration (MDC) values are approximately $0.8 \mu Bq\, m^{-3}$ and, for ^{22}Na, they are approximately $0.2 \mu Bq\, m^{-3}$. A selection of previous studies is shown in Table 2 for both of these nuclides which provides an indication of the expected aerosol concentration. Combining these typical concentrations with the MDC of the CTBT samplers, it is clear that ^{7}Be is easily detected in every daily IMS sample, while ^{22}Na is only detected on rare occasions.

3. Method

Health Canada (HC), is the federal government department responsible for Canadian radiological verification of the CTBT, analyses and collects data from all the CTBT sites that have aerosol samplers worldwide and stores the data in a LINux System for Spectral Information (LINSSI) database. From 2005 until the end of 2011, all data were stored in a *MySQL* database using the LINSSI 1.1 format (Aarnio, 2006). After this period, all data were stored in a LINSSI 2.2 database (Aarnio et al., 2011). To perform the summation, only data from LINSSI 1.1 were used as the table structure between the two versions of LINSSI are incompatible.

The technique of spectral summation was developed in an attempt to improve the ability to analyse ^{22}Na using conventional gamma spectroscopy software on the high-volume aerosol samples (approximately 20000 $m^3\ d^{-1}$ to 25000 $m^3\ d^{-1}$) of the IMS. As the ^{22}Na signal is too small to fit in a typical daily spectrum the summation process must be done before the gamma spectral analysis using the raw Multi-Channel analyser (MCA) data. In essence, the summation technique essentially performs channel-by-channel integration of the MCA output of consecutive daily samples. This is only possible because the IMS detectors are relatively stable in terms of energy calibration. However, on certain occasions the

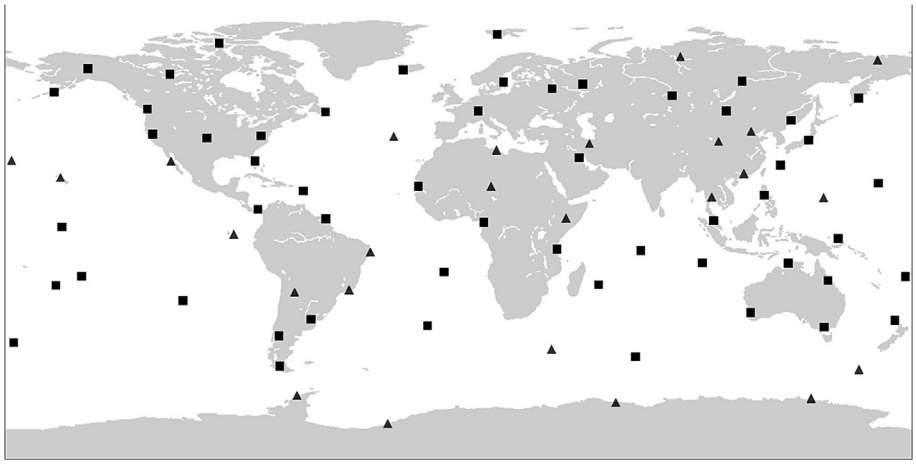

Fig. 1. Locations of Particulate Monitoring Sites of the CTBTO IMS. An increasing number of sites became available during the period of study, however some sites are still awaiting completion. Sites that contributed data to the study are shown with a square, while sites that did not contribute or were incomplete are shown with a triangle.