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The western Mediterranean basin as an aged aerosols reservoir. Insights from an old-fashioned but efficient radiotracer

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HIGHLIGHTS

- Long-term ^{210}Pb concentrations at two sites in the Mediterranean basin.
- Comparison of ^{210}Pb and PM_{10} sources at two distant sites of different altitude.
- Influence of Saharan dust transport on ^{210}Pb concentrations.
- Relevant role of the Mediterranean sea as a ^{210}Pb reservoir layer.
- Importance of aged air masses on ^{210}Pb increases in the western Mediterranean.

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ABSTRACT

The long-term contemporary ^{210}Pb time series acquired during the period 2004–2011 at two distant sites of different altitude in the Mediterranean basin, El Arenosillo (40 m a.s.l. in southwestern Spain) and Mt. Cimone (2165 m a.s.l. in northern Italy), are analyzed and compared. Besides being considered a tracer of continental air masses, ^{210}Pb radionuclide is also a proxy of fine stable aerosol. For this reason, the measurements of PM_{10} mass concentrations collected at the same time and the corresponding ^{210}Pb/PM_{10} ratio at the two sites are considered to gain better insights into the origin and size of the particles.

Three statistical trajectory methods are applied to identify and characterize the ^{210}Pb source regions at the two sites. The three methods yield similar outcomes in the source identification, which strengthens the robustness of our results. In addition to the importance of the transport from areas of continental Europe, this study highlights the relevant role of the Mediterranean Sea as a major ^{210}Pb reservoir layer associated to the aged air masses that accumulate in the western Mediterranean basin. The analysis of the sources points out the significant influence of northern Africa to ^{210}Pb increases at both sites as well, even though the most intensive episodes are not of Saharan origin.

1. Introduction

Due to its production mechanism and environmental fate, ^{210}Pb natural radionuclide has been proven as a useful tracer of continental air masses (Baskaran, 2011) and a proxy of aerosol accumulation mode, i.e., the aerosol fraction with the longest residence time in the troposphere (Hammer et al., 2007; Pio et al., 2007; Salvador et al., 2010). In fact, ^{210}Pb (half-life $\tau_{1/2} = 22.3$ years) is originated from ^{222}Rn decay ($\tau_{1/2} = 3.8$ days) mainly exhaling from the continents (Nazaroff, 1992). Once produced, ^{210}Pb rapidly attaches onto aerosol particles in the fine fraction (Papastefanou and Ioannidou, 1995; Winkler et al., 1998; Gaffney et al., 2004), and for this reason it shares with its carrier aerosol a large part of the source term and the same removal mechanisms (deposition) (Marley et al., 2000). Since ^{222}Rn oceanic input is substantially negligible, less than 1% (Nazaroff, 1992), its atmospheric concentration is mainly controlled by the sea-land distribution pattern (Balkanski et al., 1992), and for this reason its daughters ^{210}Pb and ^{210}Po are mainly longitude-dependent (Preiss et al., 1996; Baskaran,

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2011). ^{210}Pb and its daughter ^{210}Po are also the natural radionuclides with the highest contribution to the annual effective dose received by the population for ingestion and inhalation of uranium and thorium series (UNSCEAR, 2008). Due to the potential impact of ^{210}Pb on the dose rate, it is necessary to correctly identify and investigate the sources and meteorological conditions promoting its increases.

The Mediterranean Basin is recognized as a hot-spot in terms of air quality and climate change (e.g., Hesselbjerg et al., 2013) owing to both the intense pollution sources locally active as well as its geographical position between two wide continental areas resulting in a “crossroad” of different air mass transport processes (Lelieveld et al., 2002; Millán et al., 2006). Moreover, the complex topography of the Mediterranean basin and a range of different landscapes ranging from mountainous to coastal, and from fluvial plains to wetlands, plus large urban cities cause a large spatial variability of surface activity concentrations of aerosol related species and air pollutants (e.g., Hammer et al., 2007; Puustinen et al., 2007; Karanasiou et al., 2014; Tsai et al., 2015).

On a climatological basis, the western Mediterranean region is strongly affected by the arrival of air masses with strong continental influence contributing to ^{210}Pb increases (Dueñas et al., 2011; Lozano et al., 2012; Brattich et al., 2015a). Among them, it is necessary to point out the relevant influence of air masses from northern Africa: Saharan dust inputs are in fact significant contributors to the atmospheric ^{210}Pb flux by scavenging ^{210}Pb from the atmosphere during its route from Africa to the Mediterranean Sea and also during its deposition (e.g., Appleby et al., 2002; Garcia-Orellana et al., 2006; Pham et al., 2016). African dust outbreaks typically exhibit seasonal peaks during spring and summer and minima in winter and autumn (Barkan et al., 2004). With a surface area of 9,400,000 km^2 and with an estimated annual emission of 600–700 × 10^6 T (Marticorena et al., 1997), the Sahara desert is the world’s largest source of aeolian desert dust (Middleton and Goudie, 2001). Many studies have described the characteristics (background drivers, spatial and temporal variations) of Saharan air masses over the Mediterranean Basin (e.g., Querol et al., 2001; Escudero et al., 2005; Mamane et al., 2008; Papayannis et al., 2009; Koçak et al., 2012; Nava et al., 2012; Gobbi et al., 2013; Mona et al., 2014; Varga et al., 2014; Malaguti et al., 2015). Due to the intense convective injections in the Saharan desert, these air masses are frequently identified in upper atmospheric layers between 1500 and 4000 m a.s.l. (e.g., Jorba et al., 2004), where they can travel over long distances and play a key role over particulate matter (PM) ambient air levels and exceedances recorded in air quality monitoring networks in Europe (e.g., Gerasopoulos et al., 2006; Querol et al., 2009; Kabatas et al., 2014). Moreover, the Mediterranean basin is also strongly impacted by outflows of polluted European air and recirculation processes which contribute to the formation of reservoir layers for aged pollutants (e.g., Millán et al., 1996; Alper-Siman Tov et al., 1997; Tositti et al., 2013).

Despite the number of previous studies describing the origin, seasonality and behavior of atmospheric ^{210}Pb in this region (e.g., Todorovic et al., 2005; Vecchi et al., 2005; Dueñas et al., 2009; Lozano et al., 2011; Carvalho et al., 2013; Gordo et al., 2015), very few comparative analyses of simultaneous data at distinct sites have been carried out so far (e.g., Hammer et al., 2007; Lee et al., 2007). In this sense, previous studies comparing natural radionuclides at different altitudes have pointed out the likely impact of atmospheric mixing processes on the ^{210}Pb activity concentrations (Bourcier et al., 2011) and the need to describe its vertical distribution for modelling studies of dry and wet deposition, as well as to identify and compare synoptic and mesoscale patterns responsible of ^{210}Pb variations, enabling a better understanding of its global distribution.

Taking into account the potentially important role of ^{210}Pb as a proxy of fine stable (i.e., non-radioactive) aerosol this work aims at:

- Characterizing ^{210}Pb concentration and sources over the western Mediterranean Basin based on the comparative analysis the long-term contemporary time series (2004–2011) of this radionuclide recorded at two monitoring sites, namely El Arenosillo (hereafter ARE, 37.10 N, 6.70 W, 40 m a.s.l.; Spain) and Mt. Cimone (hereafter CIM, 44.20 N, 10.70 E, 2165 m a.s.l.; Italy);
- Identifying the principal air mass transport patterns at these two distinct sampling sites in the Mediterranean basin;
- Analyzing the relationship between PM$_{10}$ mass concentrations and ^{210}Pb activity concentrations in order to point out macroscopic properties of the carrier aerosol as a function of size and source.

2. Material and methods

2.1. Sampling sites

Although both the sampling stations are under the influence of the Mediterranean circulation including both natural and anthropogenic sources, they can be considered substantially remote (being separated by a geographical distance of 1600 km), and, for this reason, they present distinct meteorological features (Fig. 1). In particular, while ARE is a coastal, low-elevation site considered as a background station (Sorribas et al., 2011), CIM is a high-altitude WMO-GAW station representing free-troposphere background conditions during most of the year (Tositti et al., 2014).

ARE, which is considered a background monitoring site in Spain, is located in a fairly flat area away from industrial activities, inside a pine forest and about 1 km far from the coastline. On the contrary, CIM is located on the highest summit of the Northern Apennines, with a 360° free horizon, and fairly distant from the main pollution sources such as cities and industrialized areas both north (Po Valley) and south (Tuscan plain) of the Apenninic range.

At the synoptic scale, both sampling sites share large similarities, being both located in the Northern Hemisphere mid-latitudes where baroclinic systems are typical of the winter season (James et al., 2003), and Saharan dust outbreaks typically occur during late spring/summer (Barkan et al., 2005; Toledano et al., 2009). Considering the mesoscale, the two sites are more different: in fact, ARE area is often under the effect of sea-land breeze circulations, mainly from June to September (Adame et al., 2010), while the elevation of the CIM site is such that it lies above the atmospheric boundary layer (ABL) during most of the year, even if in particular during the warm season an influence of the innermost layer cannot be completely ruled out because of both the increased vertical mixing (thermal convection) and mountain/valley breeze regime (Fischer et al., 2003; Cristofanelli et al., 2007).

The arrival of Saharan air masses presents significantly different patterns in the Iberian Peninsula during winter and summer (Escudero et al., 2005), with a maximum frequency in the latter period (Pey et al., 2013). Specifically the characteristics and frequencies of Saharan air masses at ARE have been previously characterized (Toledano et al., 2009; Hernández-Ceballos et al., 2013a). In Italy, CIM represents the first high mountain ridge encountered by North African air masses moving to Italy and central Europe. Saharan air masses exhibit a clear annual cycle with a maximum in spring–summer and a minimum in winter (Marinoni et al., 2008; Duchi et al., 2016). Several works have studied the impact of Saharan dust advections on the properties of atmospheric aerosol at this site (Balkanski et al., 2003; Van Dingenen et al., 2005; Marenco et al., 2006; Marinoni et al., 2008; Tositti et al., 2013;