Effectiveness of airborne radon progeny assessment for atmospheric studies

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Keywords: radon progeny, radioactive atmospheric tracers, ^{210}Pb, fine aerosol residence time

Abstract

In this paper, measurements of short- and long-lived Radon progeny attached to atmospheric fine aerosols are reported.

Hourly measurements of ^{222}Rn short-lived decay products (i.e. ^{214}Bi via on-line alpha spectrometry on ^{214}Po) in the atmosphere were carried out in Milan (Italy) from 1999 to 2016; ^{214}Bi mean concentrations ranged from 0.2 to 38.1 Bq m^{-3}. It is noteworthy that minima occurred in springtime although the strongest convective turbulence can be expected in summer, when the highest solar radiation is available; one order of magnitude higher values were observed in winter when the Po valley experienced poor atmospheric dilution. The Theil-Sen method was applied to investigate the long-time trend in de-seasonalised data series. Results showed that - although inter/intra-annual variations in ^{214}Bi concentrations were observed in connection with differences in atmospheric dispersion conditions – no statistically significant trend over the investigated period was detected. On a sub-set of these samples, also weekly ^{210}Pb concentrations were determined via off-line alpha spectrometry on ^{210}Po; atmospheric activity concentration values ranged between 0.13 and 3.05 mBq m^{-3}. The seasonal behaviour of ^{210}Pb concentrations followed fairly well the ^{214}Bi temporal

pattern, showing that mixing layer dynamics is paramount in determining short- and long-lived Radon progeny levels in the atmosphere.

From $^{210}Pb/^{214}Bi$ activity ratio, the residence time τ_{res} of fine aerosols in the atmosphere was estimated to be on average 1 day, ranging from 11.0 to 55.3 h without any evident temporal trend. By exploiting the availability of mixing layer height data at our site, an alternative approach to estimate aerosol residence time was tested; this was based on a simple relationship relying on deposition velocity (from literature data) and mixing layer height (available at our monitoring station). Mean experimental τ_{res} resulted in 1.2 days which was comprised in the 0.6-2.0 days range estimated by the alternative method. This result brings a noteworthy contribution to the scientific debate about differences among aerosol residence time estimates obtained by different radioactive parent-daughter couple; our results show that the $^{210}Pb/^{214}Bi$ (or equivalently $^{210}Pb/^{222}Rn$) couple provides reliable estimates.

1. Introduction

Radon is a radioactive natural gas originating by the uranium (^{235}U and ^{238}U) and thorium (^{232}Th) decay series, which are constituents of the Earth crust. There are three radon isotopes (^{219}Rn, ^{220}Rn, and ^{222}Rn); in the following, we will refer only to ^{222}Rn (hereafter called radon), having a half-life of 3.82 days, which is long enough to follow atmospheric air masses mixing in the boundary layer. Studies on radon and its short-lived decay products (i.e. ^{218}Po, ^{214}Pb, $^{214}Bi/^{214}Po$) are of interest due to health effects related to the natural radiation exposure of the population by inhalation (ICRP, 2014; WHO, 2009). In addition, radon and its progeny have been proved to be effective tracers of atmospheric dispersion condition (e.g. Kataoka et al., 2001; Perrino et al., 2001; Sesana et al., 2003; Chambers et al., 2015; Chen et al., 2016a), air masses transport phenomena (e.g. Chambers et al., 2018; Chen et al., 2016a; and references therein), and gas fluxes in the ecosystem budget (e.g. Kooijmans et al., 2017; and therein cited literature); natural radioisotopes of terrestrial origin play

also a role in the ion production in the lower atmosphere (e.g. Chen et al., 2016b; and therein cited literature).

Information about dispersion conditions in the atmospheric boundary layer is required to improve understanding about the causes of temporal patterns observed in pollutant concentrations at different time scales (i.e. inter-annual, seasonal, and diurnal); indeed, primary pollutants level in ambient air is related to both emission source strength and atmospheric dilution. It should be taken into account that in large urban areas, it is unlikely that source emissions change a lot from one day to another (obviously long range transport phenomena are exceptions), therefore, atmospheric concentrations of air pollutants emitted by sources at ground level are largely modulated by the evolution of the atmospheric mixing layer height (MLH). Indeed, pollution episodes with values exceeding limit threshold are often recorded when poor atmospheric dilution occurs; this is typically observed e.g. for particulate matter (PM) concentrations in the Po valley – a well-known pollution hot spot in Europe. At this continental site, outdoor radon and its progeny concentrations on sunny days reach minima values during the afternoon when convective mixing in the lower layers of the atmosphere is very efficient, and maxima during the night/early morning when thermal inversions may occur thus fostering very stable atmospheric conditions and PM accumulation (see e.g. Vecchi et al., 2004; Vecchi et al., 2009). Besides the more traditional use of radon and/or its progeny concentrations for a qualitative assessment of atmospheric stability conditions, recent literature works (e.g. Griffiths et al., 2013; Salzano et al., 2016; Vecchi et al., 2019) report MLH quantitative estimates with hourly resolution based on the on-line measurement of such radioactive tracers.

To face high pollution events with effective abatement strategies, a key parameter is also the atmospheric residence time of particles which is typically not available during aerosol measurement campaigns. In the troposphere, experimental data on residence times ranging from few days to few weeks are reported with smaller values characteristic of the lower troposphere (e.g. Kristiansen et al., 2016; Papastefanou, 2006; Schmale et al., 2011; Williams et al., 2002). Aerosol residence time

estimates from models are also available, e.g. Kristiansen et al. (2016) reviewed some of them, underlying that modelling results are typically affected by large uncertainties related to the lack of observational constraints on atmospheric removal processes. An effective way to obtain aerosol residence time is the measurement of atmospheric tracers like radionuclides attached to fine aerosol particles (Porstendörfer et al., 2000), which share the same fate as atmospheric particles and are scavenged by dry or wet deposition. When using natural radioactive nuclides, it is reported that cosmogenic nuclides (e.g. ^{7}Be, see e.g Papastefanou and Ioannidou, 1995) are better suited to retrieve atmospheric particle lifetime in the upper troposphere/lower stratosphere whereas radon and its progeny can be used to estimate aerosol lifetime in the atmospheric boundary layer (e.g. Baskaran and Shaw, 2001; and therein cited literature). It is noteworthy that when ratios between radon decay products are used to obtain aerosol residence time, literature results show disagreements according to the parent-daughter couple of nuclides although much more consistent residence time values are reported when smaller-sized aerosol particles are taken into account (Baskaran, 2011; Marley et al., 2000). To give insights on this issue, in this paper aerosol residence times assessed by the ^{210}Pb/^{214}Bi couple (see Section 3.4 for details on the methodology) are compared to estimates retrieved by using literature values for the deposition velocity and MLH computed by applying a box model to ^{214}Bi concentration values (details on the model are reported in Vecchi et al., 2019).

In spite of the relevance of assessing radon and its progeny concentrations in the atmosphere, scarce long-time series of radon decay products detected with high-time resolution are still available in the literature. Multi-year data are exploited in this paper in order to: 1) provide a robust phenomenology of short- and long-lived radon progeny in the atmosphere; 2) retrieve aerosol residence times in different atmospheric conditions over the years; 3) single out possible trends in statistically significant short- and long-lived radon progeny datasets; 4) test the reliability of ^{210}Pb/^{214}Bi couple in aerosol residence times estimates in different conditions. Finally, this kind of measurements

could be useful to better interpret e.g. high pollution levels still registered in areas such as the well-known Po valley in Italy, where our monitoring station is located.

2. Experimental methodology

The measurement site is located inside our University campus in Milan (Italy), i.e. a residential area not far from the city centre. Milan (45°26' N, 9°17' E, 110 m a.s.l.) is situated in the well-known Po valley, a basin which is surrounded by the Alps to the North and by the Apennines to the South. Although being a continental area, its climate is mitigated by the influence of the Adriatic sea and by the shielding of the mountain chains; therefore, especially during wintertime, over the Po valley air masses are stagnant for most of the time and poor atmospheric dilution occurs as low wind speeds and thin mixing layer depth characterise this area.

Air sampling is performed at 6 meters a.g.l. Our group started the continuous and on-line monitoring of hourly measurements of alpha-emitting (i.e. ^{214}Po) short-lived radon decay products in 1999 and measurements are still on-going. On a sub-set of these samples, also ^{210}Pb concentrations were recovered by off-line alpha-spectrometry on 131 weekly samples collected at our monitoring site in Milan; this dataset was joined with ^{210}Pb concentration data reported in Vecchi et al. (2005) referring to the years 2000-2001 (131 samples), in order to obtain a more statistically robust dataset and perform new analyses which were not implemented in the previous work. In addition, parallel measurements of ^{222}Rn and its short-lived progeny were performed aiming at assessing the equilibrium factor. Indeed, still scarce experimental data are available on the radioactive equilibrium between radon and its daughters in the atmosphere, despite its relevance for a correct assessment of the exposure dose and for the estimate of an equilibrium factor, which is mandatory to convert short-lived decay products to radon concentration activity.

An extensive description of the experimental methodologies for measuring radon and its short- and long-lived radon decay products can be found in previous works (e.g. Sesana et al., 2003; Marcazzan et al., 2003; Vecchi et al., 2005; Vecchi et al.; 2019). An in-house computer code

performed spectra storage, peaks de-convolution, and the calculation of activity concentrations. Data analysis presented in this work was performed using the software R (R Core Team, 2019) and "openair" package (Carslaw and Ropkins, 2012).

2.1 Detection of short-lived decay products

^{214}Po activity concentrations are detected by in-house instrumentation based on continuous on-line alpha spectroscopy during the collection of atmospheric aerosol on a glass-fibre filter with a flow rate of 10 l/min; usually, each filter is changed after one week in order to avoid clogging. Indeed, ^{222}Rn decay products attached to aerosol particles emit alpha radiation that can be efficiently detected by a passivated implanted silicon semiconductor detector placed in front of the filter. Due to the very short half-life of ^{214}Po (E_α=7.686 MeV, $T_{1/2}$= 163.6 μs), in terms of activity it is substantially equivalent considering the latter or its precursor ^{214}Bi (β-emitter, $T_{1/2}$=19.9 min); therefore, in the following ^{214}Bi will be considered in accordance with previous publications by our group. Uncertainties on concentrations are mainly related to counting statistics and are estimated in about 10% and minimum detection limits are as low as 0.2 Bq m^{-3}. The latter feature is particularly interesting in atmospheric concentration monitoring, which can show very low activity values; it is also worth mentioning that a portable unit easy to operate during monitoring campaigns was realised. Additional details on short-lived progeny monitor can be found in Marcazzan et al. (2003).

2.2 Detection of long-lived decay products

^{210}Pb activity in atmospheric aerosols is detected by off-line alpha spectroscopy on weekly filter samples collected as described in Section 2.1. The measurement is carried out at delayed times (approximately after 1 year); indeed, at our laboratory measurements are conventionally performed when at least 80% of the saturation value (i.e. maximum activity) and the equilibrium activity between ^{210}Pb and ^{210}Po on the filter are reached (Figure S1, Supplementary material).

Every sample is measured for about 24 hours in a low background vacuum chamber equipped with a passivated implanted silicon semiconductor detector; further details on the experimental methodology can be found in Vecchi et al. (2005). Overall uncertainties on ^{210}Pb concentrations in the atmosphere are evaluated in 10% and the minimum detection limit is 0.02 mBq m^{-3}.

2.3 Measurements of the radioactive equilibrium factor

The radioactive equilibrium factor between radon and its short-lived daughters was assessed by parallel measurements of ^{222}Rn and ^{214}Bi. At our laboratory, an electrostatic chamber was operated to obtain ^{222}Rn atmospheric concentrations via the detection of ^{218}Po^{+} atoms; indeed, ^{218}Po is emitted by radon decay as a positive ion in 88% of the cases (Chu and Hopke, 1988). This feature is exploited by an in-house monitor operated on-line and developed following previous literature works (e.g. Costa-Ribeiro et al., 1969; Wrenn et al., 1975; Porstendorfer and Mercer, 1979). The electrostatic chamber is a semi-sphere with a 12 l volume (Figure S2). Ambient air is sampled from outdoor and then filtered and dried through a series of filters and molecular sieves before entering the electrostatic chamber. These steps are mandatory in order to get rid of particulate matter - to which radon decay products are attached - and humidity, which causes the rapid neutralisation of ^{218}Po^{+} ions (a known issue in electrostatic chambers); thus, only clean and dried air together with radon gas enter the chamber. The flowrate is set at 5 l/min in order to ensure rapid air exchange rate; this condition allows to assume that the air inside the chamber has the same radon activity concentration of ambient air. The inside surface of the chamber is painted by a Ni conductive paint which allows an electric field generation through an electrostatic voltage generator (HV=5kV). Due to this electric field, ^{218}Po^{+} ions are forced to reach a Si surface barrier detector (see Table S1 for details) which detects α particles emitted by ^{218}Po decay. The active surface of the detector is covered by a Mylar film (1.3 μm thickness) to prevent contaminations due to long-lived radon decay products. The minimum detection limit is 2 Bq m^{-3} and the overall uncertainty about 10%.

3. Results and discussion

3.1 Phenomenology of ^{214}Bi activity concentration

^{214}Bi concentration dataset comprises 152692 hourly concentrations recorded in the period January 1999–December 2016 and the overall missing data percentage is 3.2%. Activity concentrations range from 0.2 to 38.1 Bq m^{-3} (min-max). A summary of basic statistics is reported in Table 1.

^{214}Bi activity concentration (Bq m^{-3}) – period: 1999-2016			
Month	*Median*	*5th percentile*	*95th percentile*
January	10.2	3.1	20.4
February	6.5	2.0	15.9
March	4.3	1.6	12.2
April	3.5	1.5	9.9
May	3.5	1.5	10.1
June	4.0	1.8	11.4
July	4.3	2.0	12.1
August	5.3	2.3	14.9
September	5.8	2.4	15.1
October	7.6	2.9	18.1
November	8.8	3.0	20.5
December	11.5	3.3	23.5

Table 1: Basic statistics on ^{214}Bi activity concentration (in Bq m^{-3}) for the period 1999-2016.

^{214}Bi atmospheric activity concentrations over 18-years show a strong seasonal variation with higher values during winter (December-February) compared to spring (March-May) or summer (June-August) as reported in Figure S3 (where hourly concentrations are displayed); from Table 1 it is clear that maxima values occur in December-January and minima in April-May although the strongest convective atmospheric turbulence is typically expected in summer when the most intense solar radiation is available. Considering ^{214}Bi as a tracer for the dispersion conditions of the lower atmosphere, this result suggests that the better dilution of pollutants emitted at ground level occurs in springtime while during summer atmospheric dispersion is less efficient. This behaviour can be ascribed to the thermal inertia of the atmosphere as the presence of cold air masses in the upper

atmospheric layers in springtime promotes a mixing which is likely more effective than the convective mixing observed in summer, as reported in Vecchi et al. (2019).

The statistical robustness of the available dataset allows the study of time trends in ^{214}Bi atmospheric concentrations over almost two decades. The Theil-Sen estimator implemented in the Theil-Sen function available in the R "openair" package was selected to investigate the possible trend in the data series; in order to avoid the effect of the seasonality shown by ^{214}Bi concentrations, the trend was calculated on de-seasonalised data. Seasonal trend decomposition was performed using loess, which is a non-parametric method using local fittings performing least square regression (Cleveland et al., 1988). The Theil-Sen function computed monthly means from hourly data and estimated a slope which was given by the median of all slopes calculated between all available pairs of points.

In Figure 1 the monthly averages of ^{214}Bi de-seasonalised concentrations are reported together with the trend line; it is noteworthy that no significant trend is singled out over 18 years of observations. Although inter/intra-annual variation in ^{214}Bi concentration can be detected, the absence of a clear trend over the investigated period basically indicates that variations in concentrations of radon short-lived progeny in outdoor air are strongly driven by atmospheric dispersion conditions. This is a very interesting piece of information, which confirms that in our area radon short-lived progeny can be effectively used as tracer for atmospheric dispersion conditions because variations in its concentrations can be related almost entirely to atmospheric dilution effects (see e.g. Allegrini et al., 1994; Sesana et al., 2003; Vecchi et al., 2019).

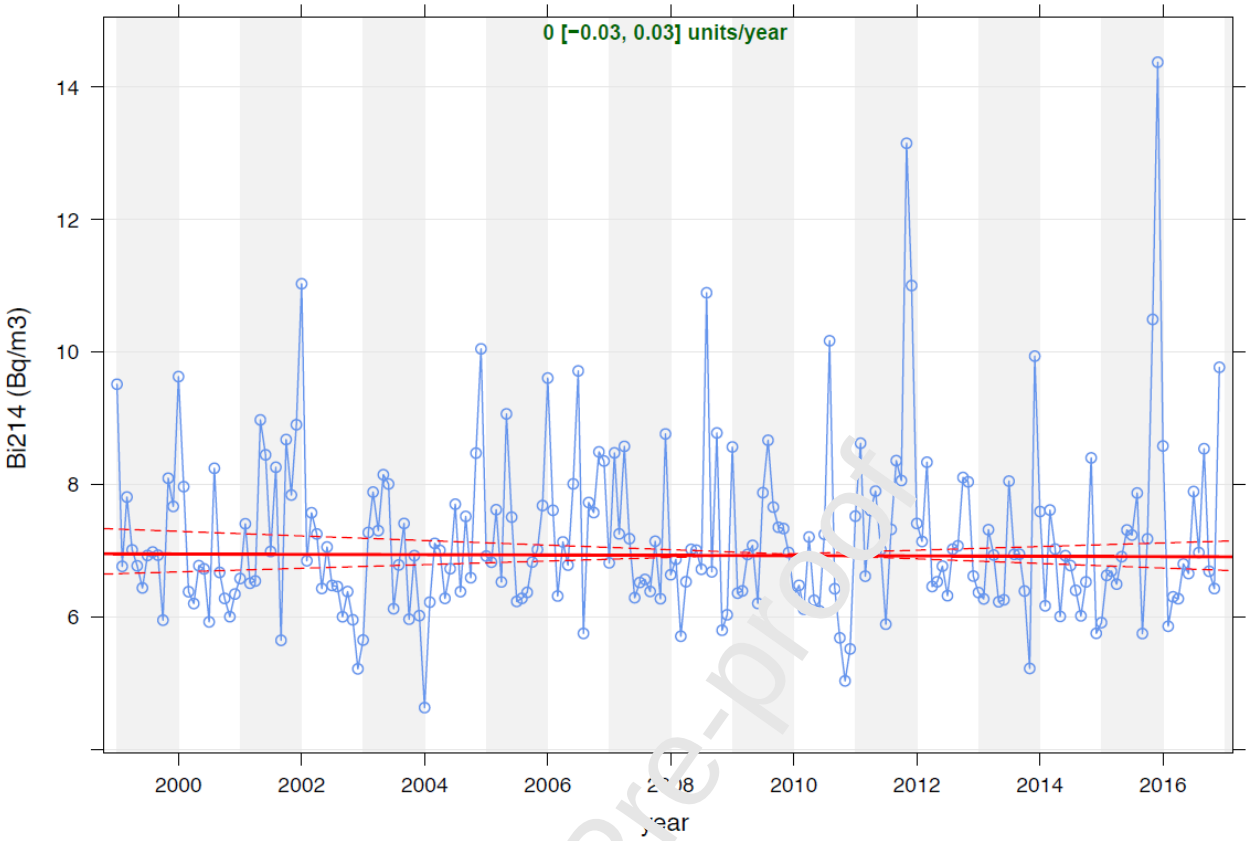

Figure 1: Time trend analysis of ^{214}Bi activity concentrations during the period 1999-2016 applied to de-seasonalised data. The blue circles indicate monthly averages of ^{214}Bi de-seasonalised concentrations (in Bq m^{-3}), the solid red line shows the trend estimate, and the dashed red lines show the 95% confidence intervals for the trend based on resampling methods. The overall trend is shown at the top as 0 Bq m^{-3} per year, together with the 95% confidence interval [-0.03 – 0.03].

^{214}Bi concentrations reported by year and hour of the day in Figure S3 are typically lower than 10-12 Bq m^{-3} and show only small differences in minima values; however, in winter months much higher activity concentrations (up to 20-22 Bq m^{-3}) are recorded especially in 2011 and 2015 (this is also evident in maxima values in Figure 1). High ^{214}Bi concentrations point at strong atmospheric stability conditions, which also affected pollution levels in the urban area. Indeed, in December 2015 the atmosphere was characterised by a very poor dilution power as can be seen by mixing layer heights retrieved by the turbulence-based approach (details about the modelling approach are

reported in Vecchi et al., 2019) for the same month in the years 2012-2016 when sonic anemometer data were available. Considering MLH average on the time interval 10:00-17:00 UTC+1h, i.e. the period of the day when the boundary layer is supposed to be well mixed, the maximum MLH for December 2015 was 324 m while it ranged from 533 to 802 in December on 2012, 2013, 2014, and 2016 (Figure S4). The same analysis is not carried out for winter 2011 since MLH data are not available.

An example of the effect of atmospheric stability on pollution levels at our monitoring site can be seen looking at daily PM10 concentrations (i.e. particulate matter with an aerodynamic diameter less than 10 μm, data available from the monitoring network of the regional environmental agency, ARPA Lombardia); indeed, in December 2015 daily PM10 values exceeded the European limit value of 50 $\mu g/m^3$ in 27 days out of 35 per year allowed by EU air quality standards. PM pollution registered in Milan on December 2015 was promoted by very poor atmospheric dilution (average MLH was 187 metres during the time interval 10:00-17:00), scarce precipitation (monthly cumulative rainfall was 0.6 mm), and low wind speed (only 5% of hourly wind data were higher than 2 m s^{-1}).

The mean daily patterns of ^{214}Bi represented in Figure 2 for each season reveal the well-known "thermal wave" showing maxima in the morning and minima during the afternoon (Garzon et al., 1986); this peculiar feature is well explained by the modulation of the mixing layer height in the atmospheric boundary layer (e.g. Kataoka, 1998; Sesana et al., 2003). The maximum-to-minimum time interval is different going from summertime to wintertime in agreement with the time interval between sunrise and sunset which varies from month to month.

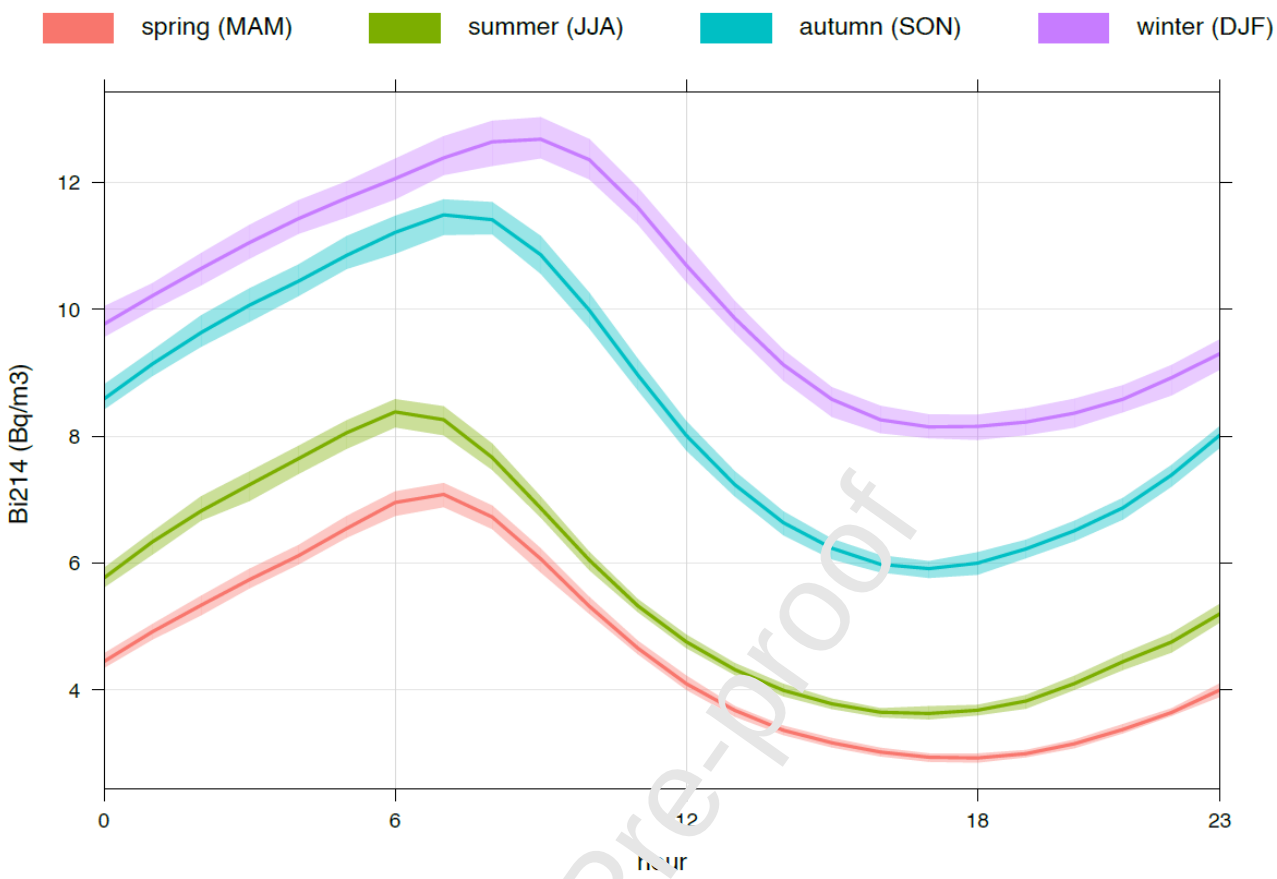

Figure 2: ^{214}Bi typical daily patterns calculated on the whole dataset (1999-2016) and represented separately for different seasons (x-axis is UTC+1h).

3.2 From ^{214}Bi to ^{222}Rn activity concentration: assessment of the radioactive equilibrium factor

The phenomenology of ^{214}Bi discussed so far can be easily adapted to ^{222}Rn activity concentration when a suitable radioactive equilibrium factor is available for the monitoring site; indeed, this factor shows a large variability depending on the site characteristics, meteorology, and season. The equilibrium factor can be calculated as the ratio between ^{222}Rn and its progeny activity concentration when ^{222}Rn decay products are considered in equilibrium in the atmosphere. Parallel ^{214}Bi and ^{222}Rn measurements were performed in Milan (November 2000 – February 2001) to retrieve a site-specific equilibrium factor and in Figure 3 the two data series are reported. They are highly correlated (R^2=0.98) and the median equilibrium factor is 0.76 (interquartile range: 0.70 – 0.86). Outliers with values higher than 1.2 are registered in 0.3% of the cases only and are always

associated to periods with strong winds or heavy rainfalls when the equilibrium hypothesis does not hold.

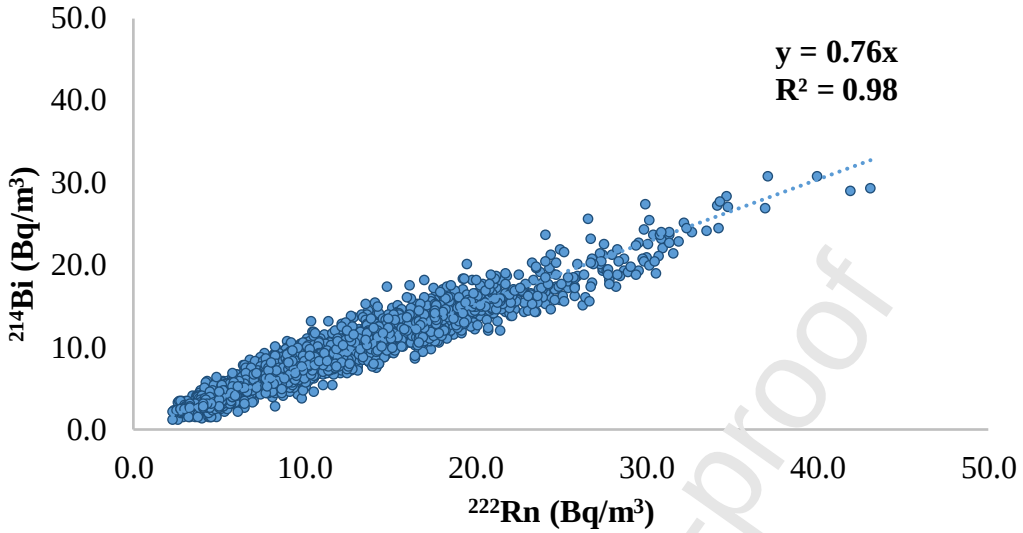

Figure 3: Relationship between ^{214}Bi and ^{222}Rn concentrations in Milan (data collected in the period of November 2000 – February 2001).

3.3 ^{210}Pb activity concentrations in outdoor air

Atmospheric ^{210}Pb activity concentrations range from 0.13 to 3.05 mBq m^{-3} (min-max); average monthly values are reported in Table 2. At our monitoring site, ^{210}Pb activity concentration values are lower in spring and at the beginning of summer (March-July) and higher in autumn and winter (October-January). Similar results are also found at other European sites (e.g. Paatero et al., 1998; Sýkora et al., 2017; Winkler and Rosner, 2000) and in Middle East locations (e.g. Ahmed et al., 2004; Mohery et al., 2016). Nevertheless, there are sites where ^{210}Pb activity concentrations show an opposite behaviour, reaching maxima during summer months (e.g. in Spain, Dueñas et al., 2009; García-Talavera et al., 2001); this different pattern can be ascribed to a different climatology often influenced by air mass transport (Dueñas et al., 2011) which is not the case at our monitoring site.

Month	**^{210}Pb [mBq m^{-3}]**	**Samples**
January	1.14 ± 0.43 (0.35 - 1.79)	24
February	0.80 ± 0.45 (0.13 - 2.02)	30
March	0.58 ± 0.31 (0.17 - 1.30)	30
April	0.39 ± 0.15 (0.17 - 0.75)	24
May	0.56 ± 0.19 (0.21 - 1.13)	27
June	0.61 ± 0.29 (0.17 - 1.46)	25
July	0.57 ± 0.21 (0.28 - 1.02)	20
August	0.79 ± 0.28 (0.35 - 1.32)	16
September	0.71 ± 0.43 (0.26 - 2.09)	16
October	1.06 ± 0.47 (0.24 - 2.15)	17
November	1.09 ± 0.56 (0.33 - 1.99)	15
December	1.39 ± 0.67 (0.30 - 3.05)	18
Overall mean value	0.78 ± 0.47	262

Table 2: ^{210}Pb monthly activity concentrations for the years 1999 - 2002 and 2011 - 2015 (in mBq m^{-3})

As previously discussed for ^{214}Bi data, also ^{210}Pb average monthly concentrations (Table 2) show minima in springtime and maxima in wintertime, although ^{210}Pb is characterised by concentrations 10^4 times lower than ^{214}Bi ones. In Figure 4 activity concentrations of ^{214}Bi and ^{210}Pb show similar temporal patterns in the atmosphere (Pearson correlation coefficient R=0.88) as also reported in other literature studies (Kim et al., 2000; Sýkora et al., 2017). According to Kim et al. (2000), such correlation is a proof-of-evidence of the steady-state assumption which is needed for the box model used to calculate aerosol residence time (see Section 3.4).

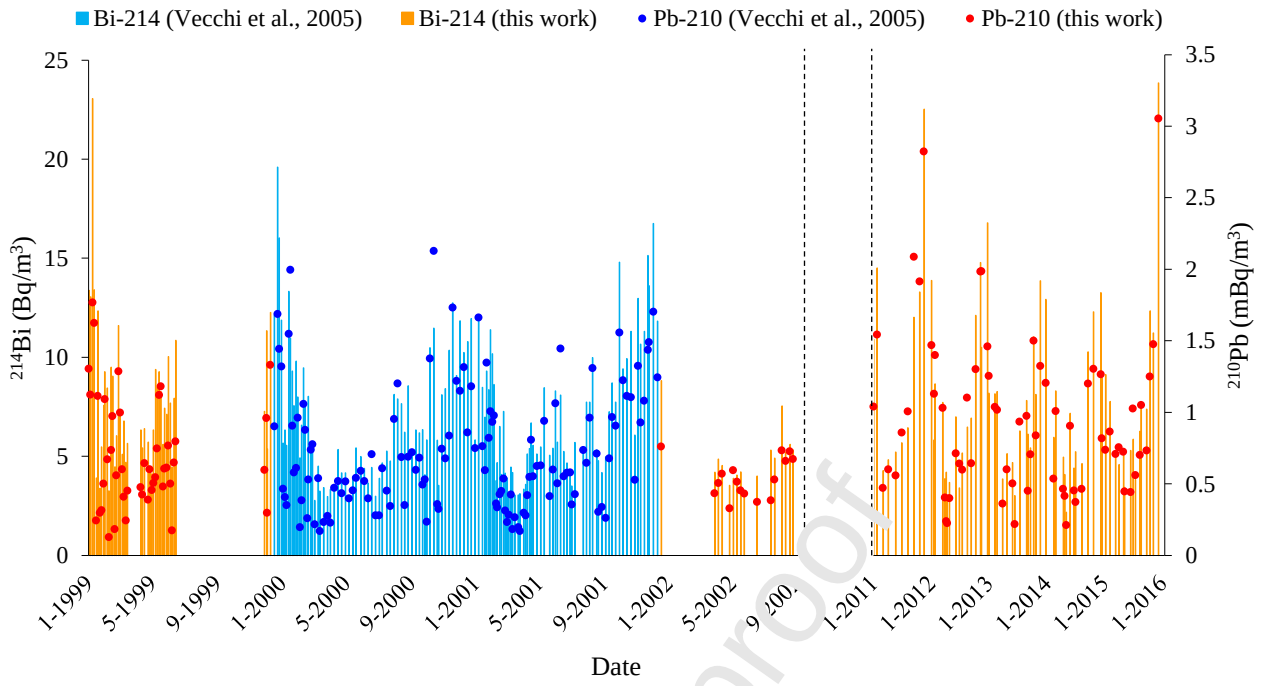

Figure 4: Temporal patterns of ^{214}Bi (left scale in Bq m^{-3}, represented as bars) and ^{210}Pb (right scale in mBq m^{-3}, represented as dots). Please note that the x-axis is divided into two periods (1999-2002 and 2011-2015).

3.4 Aerosol residence time

Aerosol residence time in the atmosphere can be assessed estimating the disequilibrium between the activity concentrations of a radon decay product (called "parent") and the isotope produced by its decay (called "daughter"). Widely used are daughter-parent couples composed of two long-lived nuclides (e.g. ^{210}Bi/^{210}Pb, ^{210}Po/^{210}Pb) or by a long and a short-lived nuclide or radon (e.g. ^{210}Pb/^{214}Bi, ^{210}Pb/^{222}Rn). In the hypothesis of an atmospheric isolated and well-mixed system where ^{222}Rn exhalation rate can be considered constant, the rate of change in daughter nuclei is given by the following equation (Baskaran, 2011; Baskaran and Shaw, 2001):

$$\frac{dN_d}{dt} = \lambda_p N_p - \lambda_d N_d - \lambda_r N_d \qquad (1)$$

where N_d and N_p are daughter and parent concentrations (in atoms m^{-3}), respectively; λ_d and λ_p are their decay constants (in s^{-1}).

It is worthy to note that the term $\lambda_r N_d$ would not be present in the equation in case of removal due to radioactive decay processes only, but it is here added to take into account the effect of atmospheric deposition of the daughter nuclei attached to aerosol particles. Indeed, the λ_r term represents the decay constant of the removal rate and it is the inverse of the residence time (τ_{res}).

Radon exhalation varies slowly in space and time as reported e.g. by Porstendörfer (1994); as an example, from the European emission inventory given by Szegvary et al. (2009), a constant exhalation rate can be roughly estimated in the area investigated in this work, thus supporting the steady-state assumption.

Following the methodology reported in literature works (e.g. Gäggeler et al., 1995; Vecchi et al., 2005), the residence time (τ_{res}) of atmospheric aerosols was estimated using the couple $^{210}Pb/^{214}Bi$ in the approximation of a simple steady-state model. With this assumption, the left-hand side of equation (1) becomes null; thus, equation (1) can be re-written as:

$$0 = \lambda_{Bi-214} N_{Bi-214} - \lambda_{Pb-210} N_{Pb-210} - \frac{1}{\tau_{res}} N_{Pb-210} \qquad (2)$$

By multiplying equation (2) for $\lambda_{Pb\text{-}210}$ and by expressing $\lambda_{Bi\text{-}214}N_{Bi\text{-}214}$ and $\lambda_{Pb\text{-}210}N_{Pb\text{-}210}$ as activity concentrations $C_{Bi\text{-}214}$ and $C_{Pb\text{-}210}$ respectively, the expression for aerosol residence time is obtained:

$$\tau_{res} = \frac{C_{Pb-210}}{C_{Bi-214}} \cdot \frac{1}{\lambda_{Pb-210}\left(1 - \frac{C_{Pb-210}}{C_{Bi-214}}\right)} \qquad (3)$$

It is important to recall that τ_{res} is the residence time of aerosol particles belonging to the accumulation mode (aerodynamic diameter ranging from 0.1 to 1 μm) since the largest radon progeny activity fraction is attached to particles in this size range (Porstendörfer et al., 2000).

Residence times (given in hours) are reported in Figure 5 for the two datasets merged in this work in order to obtain a more robust statistical assessment. The variability observed in these data has been studied in relation to meteorological parameters (wind speed, precipitation, temperature, and relative humidity); however, no statistically significant difference has been found in aerosol residence times referring to periods characterised by different meteorological conditions. This can

be ascribed to the fact that residence times are computed over weekly samples, which often include a mixture of different meteorological conditions.

Although residence times referring to years 2011-2015 are significantly higher than those referring to years 1999-2002 as shown by Mann-Whitney test (Hollander and Wolfe, 1999), giving p-value < 0.01, possible temporal trends in data series are not investigated in this work, since samples are not equally time-spaced (see Table 3) and a greater number of measurements related to years 2011-2015 would be necessary to perform robust trend analysis.

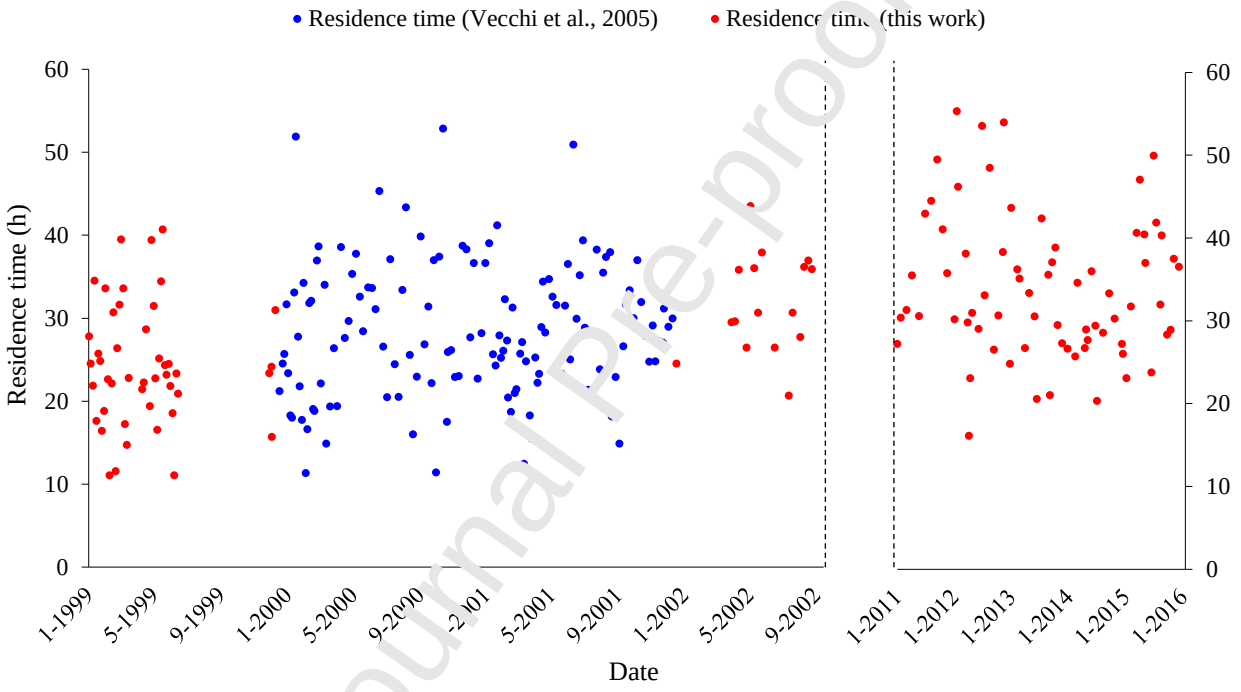

Figure 5: Aerosol residence times (h). Please note that the x-axis is divided into two periods (1999-2002 and 2011-2015).

Year	Number of samples
1999	45
2000	65
2001	66
2002	16
2011	10
2012	16
2013	15
2014	14
2015	15

Table 3: Number of samples obtained for the years 1999-2002 and 2011-2015.

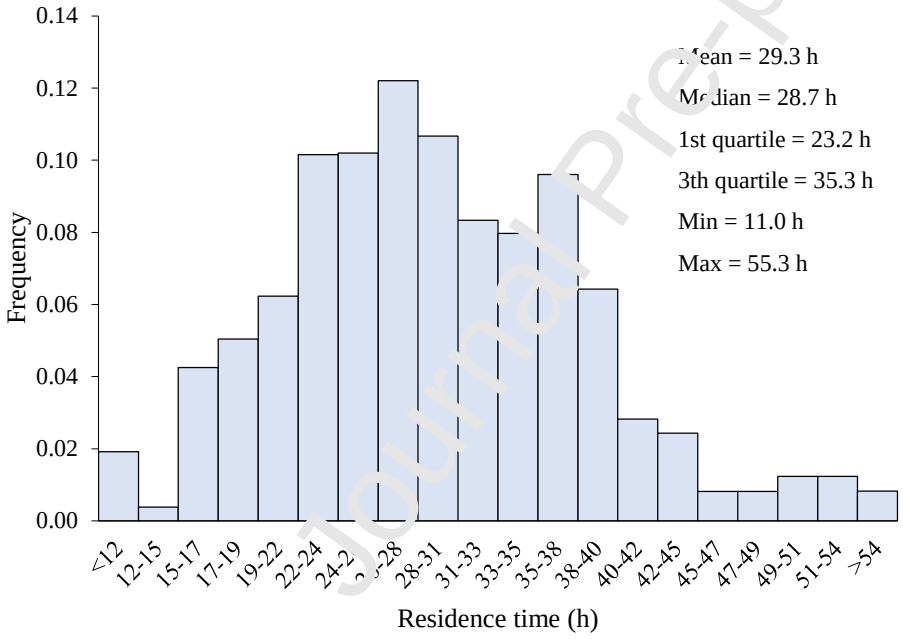

Figure 6: Frequency distribution of aerosol residence times.

The frequency distribution of residence times is quite symmetric (Figure 6); the interquartile range is 23.3 – 35.3 h with a median atmospheric residence time of 28.7 h. From Table 4, it can be seen that there is not a remarkable seasonality in average monthly residence times and the overall average of aerosol residence times is 29.3 ± 8.6 h, in accordance with those found at other sites

using the couple $^{210}Pb/^{222}Rn$ (1-5 days, e.g. Kim et al., 2000; Sýkora et al., 2017). Aerosol residence times from about 1 to 15 days are reported for Middle East locations using the $^{210}Pb/^{214}Pb$ couple, (Ahmed et al., 2004; Mohery et al., 2016); however, the authors report that the longer residence times can be ascribed to the regional weather conditions characterised by hot southerly winds loaded with dust particles.

Month	**Aerosol residence time [h]**	**Samples**
January	27.3 ± 6.4 (18.0 - 43.6)	24
February	27.8 ± 10.7 (11.0 - 55.3)	30
March	26.6 ± 8.8 (11.5 - 40.6)	30
April	26.1 ± 7.4 (15.5 - 47.[illegible])	24
May	31.3 ± 6.2 (16.5 - 43.5)	27
June	28.8 ± 8.2 (11.0 - 50.9)	25
July	33.2 ± 10.4 (20.3 - 53.5)	20
August	33.1 ± 8.0 (20.5 - 48.4)	16
September	29.4 ± 10.1 (14.9 - 49.4)	16
October	32.5 ± 8.4 (11.4 - 52.8)	17
November	30.1 ± 9.1 (17.5 - 53.9)	15
December	29.5 ± 5.9 (15.7 - 38.7)	18
Overall mean value	29.3 ± 8.6	262

Table 4: Monthly aerosol residence times for the years 1999-2002 and 2011-2015 (in hours).

It is worth recalling that in the literature great discrepancies are typically found in residence times calculated using different parent-daughter couples (Anand and Mayya, 2015; Baskaran, 2011; Jia, 2014; Papastefanou, 2009, 2006; Turekian et al., 1977; and therein cited literature). Indeed, $^{210}Pb/^{214}Bi$, $^{210}Pb/^{214}Pb$, and $^{210}Pb/^{222}Rn$ couples often provide residence times of the order of few days up to one week (Aba et al., 2020; Ahmed et al., 2004; Bikkina et al., 2015; Gäggeler et al., 1995; Kim et al., 2000; Mohery et al., 2016; Rastogi and Sarin, 2013; Sýkora et al., 2017), $^{210}Bi/^{210}Pb$ ratio yields to values of approximately 1-2 weeks (Długosz-Lisiecka and Bem, 2012; Marley et al., 2000; Papastefanou, 2009, 2006; Papastefanou and Bondietti, 1991), and finally the

couple $^{210}Po/^{210}Pb$ provides much longer residence times, of the order of a month and more (Baskaran and Shaw, 2001; Długosz-Lisiecka and Bem, 2012; Jia, 2014; Kim et al., 2000; Marley et al., 2000; McNeary and Baskaran, 2007). Other couples are rarely used in the literature; e.g. (Turekian et al., 1999) estimated a residence time of 16 hours from the couple $^{214}Bi/^{214}Pb$.

To face the debate about which couple is better suited to estimate aerosol residence time, critical issues regarding these couples have been considered and studied in some literature works. Firstly, it is widely reported that the couple $^{210}Po/^{210}Pb$ overestimates residence time due to the volatile nature of ^{210}Po and its consequent sensitivity to both natural and artificial additional sources, such as resuspended soil dust, volcanic eruptions, biomass burning, and fossil fuel combustion (Długosz-Lisiecka, 2016; Długosz-Lisiecka and Bem, 2012; Jia, 2014; Lozano et al., 2011; Papastefanou, 2006).

Other few literature works (Junge, 1963; Rastogi and Sarin, 2013; Turekian et al., 1977) outline that residence time assessment from the couple $^{210}Pb/^{222}Rn$ (and similarly from $^{210}Pb/^{214}Pb$ and $^{210}Pb/^{214}Bi$) requires the assumption of a constant radon exhalation rate. However, many external factors - such as meteorology conditions and soil porosity - affect radon flux which can show significant spatial and temporal variability in specific regions. Thus, this hypothesis should be verified to obtain reliable residence time values when using the mentioned couple.

As concerns the couple $^{210}Bi/^{210}Pb$, it is generally reported (e.g. Długosz-Lisiecka and Bem, 2012; Jia, 2014; Papastefanou and Bondietti, 1991; Turekian et al., 1977) that it produces more robust residence time estimates compared with the couple $^{210}Po/^{210}Pb$ because ^{210}Bi has a short half-life (about 5 days), which makes this radionuclide less sensitive to external sources. Nevertheless, the couple $^{210}Bi/^{210}Pb$ provides residence times which are typically longer than those obtained with $^{210}Pb/^{222}Rn$, but it is not straightforward to find in the literature papers comparing results from these couples.

To check the reliability residence time τ_{res} assessment obtained by the $^{210}Pb/^{214}Bi$ couple through equation (3), aerosol lifetime has been derived in this work using also an alternative and

independent approach based on the relationship between the residence time and the deposition velocity. Following Wiman et al. (1990), aerosol residence time can be expressed as the ratio of the scale height H of atmospheric aerosol - which is frequently approximated by the MLH - to a loss function governed by atmospheric removal processes and ground surface mechanism and identified as the deposition velocity v_D as follows:

$$\tau_D \sim \frac{H}{v_D} \qquad (4)$$

By exploiting the attachment of ^{210}Pb to aerosol particles (or any other aerosol-attached radionuclide), aerosol deposition velocity can be obtained by the ratio of the total nuclide deposition flux F (Bq m^{-2} s^{-1}) to its atmospheric activity concentration C (Bq m^{-3}) (Baskaran, 2011). With these assumptions, it should be noted that v_D relates only to aerosol particles belonging to the accumulation mode - to which the most of radon progeny activity is associated – whose dominant removal processes are wet and dry deposition.

In this work, τ_D is calculated for each of the 262 weekly samples by equation (4) and is compared to τ_{res} retrieved by equation (3). Hourly mixing layer heights computed as in Vecchi et al. (2019) are available from our research group so that the weekly average of MLH daily maxima is assigned to each sample as scale height; for the investigated periods, weekly MLH ranges from about 100 to 2300 m with a median value of 998 m. Unfortunately, v_D values corresponding exactly to our weekly samples are not available; therefore, literature values reviewed by Baskaran (2011) are used to estimate aerosol residence time using equation (4). Average v_D ranges from 0.6 to 1.9 cm s^{-1} and these two extreme values are taken into account to roughly estimate τ_D. It is worthy to note that in the literature works these v_D values are referred to as the total deposition velocity, which relates to both wet and dry deposition; therefore, they are suitable to our purpose, as samples are characterised by meteorological conditions which often vary from day to day during the sampling week. Results were compared to those obtained in this work using the couple ^{210}Pb/^{214}Bi in the approximation of an atmospheric isolated sample at steady-state. Mean τ_D derived from equation (4)

ranges from 0.6 to 2.0 days when v_D minima (0.6 cm s^{-1}) and maxima (1.9 cm s^{-1}), respectively, literature values are used; the agreement with τ_{res} experimentally obtained in this work is fairly good (Table 5) as it falls in the middle of the range. Even when the minimum value of v_D is considered, τ_D is less than 5 days. This is a relevant piece of information to the literature debate about the robustness of aerosol residence times estimated by different parent-daughter couples.

	τ_D [d] for v_D min (0.6 cm s^{-1})	τ_D [d] for v_D max (1.9 cm s^{-1})	τ_{res} [d] obtained in this work
Mean	2.0	0.6	1.2
1st quartile	1.3	0.4	1.0
Median	1.9	0.6	1.2
3rd quartile	2.6	0.8	1.5
Min	0.3	0.1	0.5
Max	4.4	1.4	2.3

Table 5: Basic statistics of residence time τ_D obtained by equation (4), compared with residence time τ_{res} computed by equation (3).

4. Conclusions

In this work, it has been shown that radon short- and long-lived decay products are effective atmospheric radioactive tracers and the measurement of their activity concentration allows to assess atmospheric dilution conditions and residence times of aerosols in the accumulation mode. Hourly ^{214}Bi activity concentrations range from 0.2 to 38.1 Bq m^{-3} in the 1999-2016 period. It is interesting to note that over almost 2 decades no significant long-term trend is found although in a couple of cases (wintertime 2011 and 2015) it is clear the occurrence of much higher ^{214}Bi levels linked to stronger atmospheric stability conditions. Interestingly, minima concentrations are observed in April-May thus suggesting that the most efficient atmospheric dispersion is registered in springtime at our site. This is a relevant result as typically the highest atmospheric mixing in the boundary layer is expected in summer when solar radiation availability promotes the production of

thermals. Therefore, monitoring radon short-lived decay products can be effective in following the evolution of the atmospheric dilution power and helpful in interpreting e.g. trends in pollution levels.

From ^{210}Pb activity concentrations measured on weekly samples and ^{214}Bi concentrations averaged over the same time intervals, fine aerosol residence time can be calculated by using the simple steady-state model based on ^{210}Pb/^{214}Bi couple. The mean residence time assessed on 262 samples is 29.3 ± 8.6 h. Since great discrepancies are generally found in residence times obtained by different parent-daughter couples, an alternative estimate of aerosol lifetime has been derived by the relationship between the aerosol scale height and the deposition velocity, by exploiting the availability of mixing layer heights data at our site and literature deposition velocity values. It ranges from about half to two days in dependence of the deposition velocity taken into account; the longest τ_D estimated is less than 5 days (i.e. in agreement with the experimental values obtained in this work) thus suggesting that the ^{210}Pb/^{214}Bi couple is a good choice for assessing fine aerosol residence times and the use of ^{210}Bi/^{210}Pb or ^{210}Po/^{210}Pb likely produce an overestimate.

It is noteworthy that assessment of aerosol residence times is useful for the correct interpretation of high pollution events and the effectiveness of related abatement strategies or the study of processes in which aerosols can be involved in once emitted in the atmosphere.

Acknowledgements

The authors are grateful to all students who performed part of the measurements during their Bachelor or Master Degree Thesis. Authors are thankful to dr. Patrizia Favaron for collaborative work related to MLH estimates from sonic anemometer data. ARPA Lombardia is acknowledged for meteorological and pollution data availability.

INFN (National Institute of Nuclear Physics) and the Università degli Studi di Milano (University Research Program PUR) are acknowledged for the financial support given.

The authors are indebted to Dr. Dario Colosimo, his family, and to the Department of Physics (Università degli Studi di Milano) for the fellowship grant to Dr. Crova, which allowed to finalise this work.

Author contributions

Federica Crova: Writing Original Draft - Investigation - Formal Analysis. **Gianluigi Valli**: Methodology - Software-Data curation - Investigation. **Vera Bernardoni**: Formal Analysis - Writing Review & Editing. **Alice Corina Forello**: Visualization - Writing Review & Editing. **Sara Valentini**: Validation - Writing Review & Editing. **Roberta Vecchi**: Conceptualization - Writing Review & Editing - Supervision - Funding acquisition.

Data availability

The data of this study are available from the corresponding author upon request (roberta.vecchi@unimi.it).

Declaration of competing interest

The authors declare no conflict of interest.

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Author contributions

Federica Crova: Writing Original Draft - Investigation - Formal Analysis. **Gianluigi Valli**: Methodology - Software-Data curation - Investigation. **Vera Bernardoni**: Formal Analysis - Writing Review & Editing. **Alice Corina Forello**: Visualization - Writing Review & Editing. **Sara Valentini**: Validation - Writing Review & Editing. **Roberta Vecchi**: Conceptualization - Writing Review & Editing - Supervision - Funding acquisition.

Highlights:

- Natural radioactive isotopes are effective tracers to study atmospheric processes
- Fine aerosol residence times retrieved through long- and short-lived Radon progeny
- Fine aerosol residence times in Milan ranged between 11 and 55 hrs
- Residence time reliability assessed by deposition velocity and mixing layer height