

Atmospheric Residence Times of the Fine-aerosol in the Region of South Italy Estimated from the Activity Concentration Ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in Air Particulates

Guogang Jia^{1*} and Jing Jia²

¹National Institute of Environmental Protection and Research, Via V. Brancati 48, 00144 Roma, Italy

²Roma Third University, Via Corrado Segre 4/6, 00146 Roma, Italy

Abstract

The activity concentrations of ^{210}Po and ^{210}Pb in atmospheric particulate samples collected in South Italy (Taranto) in Nov 2008 and in May 2009 were determined. The corrected activity concentrations of ^{210}Pb and ^{210}Po in sampling time were in the range of 11.9-122 $\mu\text{Bq m}^{-3}$ and of 300-1105 $\mu\text{Bq m}^{-3}$, respectively. The $^{210}\text{Po}/^{210}\text{Pb}$ activity concentration ratios were in the range of 0.0273-0.174. Based on the $^{210}\text{Po}/^{210}\text{Pb}$ activity concentration ratios in air particulates, the atmospheric residence times of aerosol in South Italy were estimated, which are ranged from 8.89 to 49.7 days. The calculated residence times are very useful for simulating and modeling the atmosphere transport process of the inorganic and organic pollutants in air in the studied region.

Keywords: ^{210}Pb ; ^{210}Po ; Aerosol; Air; Atmospheric particulate; Residence time

Introduction

Since long-range atmosphere transport is one of the major pathways of pollutants, studies on the fate and transport of inorganic and organic atmosphere pollutants are potentially significant. Aerosol-active radionuclides are ideal tracers for the study of atmosphere transport processes of troposphere and stratosphere aerosols. These radioactive tracers can be classified into three different groups according to their origin: (1) cosmogenic radionuclides (^7Be , ^{22}Na , ^{32}P , ^{33}P , ^{35}S , etc.), which are produced in the upper atmosphere (stratosphere and troposphere) by spallation processes of light atomic nuclei (e.g. nitrogen and oxygen) when they absorb primary (mostly protons) and secondary (neutrons) cosmic radiation [1-5]; (2) artificial radionuclides (^{89}Sr , ^{90}Sr , etc.), produced by nuclear weapons tests, nuclear power plants, nuclear fuel reprocessing facilities, even some nuclear accidents [6,7]; and (3) natural radionuclides (^{222}Rn , ^{210}Pb , ^{210}Bi , ^{210}Po , etc.), produced during element evolution in the earth [8-11].

Due to the fact of continuous existence in the atmosphere, the natural radionuclides (^{222}Rn , ^{210}Pb , ^{210}Bi , ^{210}Po) have widely been used as powerful and preferable tracers to study the atmosphere transport processes of aerosols. It was reported that more than 99% of the ^{222}Rn in the atmosphere are derived from emanation mainly from the continents. Once the ^{222}Rn escapes from the rocks and minerals in the upper crust of the earth, it starts its journey in the atmosphere via diffusion and advection [12]. On its pathway, some of ^{222}Rn undergo radioactive decay. The atmospheric ^{222}Rn is not removed by either physical or chemical means due to its inert nature. The mean life of ^{222}Rn (τ : 5.53 d) is comparable to the transit time of air masses across major continents and/or ocean, but much shorter compared to the mixing time scale of the atmosphere, and hence, it is widely dispersed in the atmosphere. The activities of the long-lived progenies, ^{210}Pb , ^{210}Bi and ^{210}Po in the atmosphere to a large extent are governed by their production rates, rates of radioactive decay and removal by atmospheric aerosol scavenging.

Over the past six decades, the distribution of ^{222}Rn and its progenies (^{210}Pb , ^{210}Bi , ^{210}Po) have provided very rich information as tracers to quantify several atmospheric processes in the aspects of (1) source

tracking and transport time scales of air masses, (2) removal rate constants and residence times of aerosols, (3) stability and vertical movement of air masses, (4) physical and chemical behavior of analog species, and (5) washout ratios and deposition velocities of aerosols [4,8,9,11-17].

The tropospheric residence times are variable and are largely affected by the climate. In this paper, ^{210}Po and ^{210}Pb were utilized as atmospheric tracers and the residence times of aerosol in South Italy were calculated based on the activity concentration ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in air. This is a preliminary attempt in the region of South Italy (Mediterranean Sea). The calculated residence times were compared with that reported in other regions by other researchers and the discordant residence times of aerosols were discussed. The obtained data are very useful for simulating and modeling the atmosphere transport process of the inorganic and organic pollutants in air in the studied region.

Materials and Methods

Apparatus and reagents

Bismuth-210 for ^{210}Pb determination was measured by a 10-channel low-level β -counter (Berthold LB770, Germany). The instrument and reagent background of the counter for ^{210}Pb measurement is of ≤ 0.0053 cps and the counting efficiency was 48.2% that was calibrated with a PbSO_4 precipitate source obtained from a standard ^{210}Pb solution. ^{210}Po was determined by alpha spectrometry (Canberra, U.S.A.) with a counting efficiency of 31.2% and a background of $\leq 6 \times 10^{-6} \text{ s}^{-1}$ in the interested energy region.

***Corresponding author:** Guogang Jia, National Institute of Environmental Protection and Research, Via V. Brancati 48, 00144 Roma, Italy, Tel., Email: guogang.jia@apat.it

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A Perspex disk holder for polonium deposition was specially designed to fit 100-250 ml beakers [18]. Silver foil with a thickness of 0.15 mm was used for ^{210}Po spontaneous deposition and it was cut into disks of 23 mm in diameter. Large volume air sampler was the Model Thermo G10557 equipped with analyzer of $\text{PM}_{2.5}$ or PM_{10} .

Polonium-209 solution standard as a tracer for ^{210}Po determination by α -spectrometry and ^{210}Pb solution standard for β -instrument calibration, the reference material (IAEA-315) for quality control and the BIO-RAD-AG 1-X4 resin (100-200 mesh) for Pb separation were supplied by the Amersham (UK), the IAEA and the Bio-Rad Laboratories (Canada), respectively. $\text{Pb}(\text{NO}_3)_2$ to prepare the carrier solution for Pb separation and all other reagents were analytical grade.

Sites and sampling

Italy is a peninsula state in Mediterranean Sea surrounded by Tirreno Sea, Ionio Sea and Adriatico Sea, and has a very mild climate with rich precipitation in north and center, and less rich precipitation in south. The most sampling sites were located at near Taranto City and one site at the Castel Romano of Roma (CSM Roma), south of Italy. For determination of the residence time of the aerosol, atmospheric particulate samples were collected in 11-29 Nov, 2008 (the first sampling campaign) and in 4-9 May 2009 (the second sampling campaign). The atmospheric particulate samples were taken by a large volume (about $67 \text{ m}^3 \text{ h}^{-1}$) sampler. The sampler was equipped with an analyzer of $\text{PM}_{2.5}$ or PM_{10} and can collect the atmospheric particulate of aerodynamic diameters $\leq 2.5 \mu\text{m}$ ($\text{AP}_{2.5}$) or $\leq 10 \mu\text{m}$ (AP_{10}) with a glass-microfiber filter of dimensions of $20 \text{ cm} \times 25 \text{ cm}$ (Whatman GF/A cat. N. 1820-866). During sampling, the velocity of the air for both samplers was about $1 \text{ m}^3 \text{ min}^{-1}$. The detailed information about the sampling sites was given in Tables 1 and 2. It was assumed that the collection efficiency for ^{210}Po and ^{210}Pb were constant and same. In such a case, problems

in collection efficiency will not affect the residence time of aerosols, calculated from the activity concentration ratios of $^{210}\text{Po}/^{210}\text{Pb}$.

Anion-exchange resin column preparation

The anion-exchange resin, BIO-RAD-AG 1-X4 (100-200 mesh), was sequentially treated with 6 M NaOH, 6 M HCl and distilled water to remove any fine particles as well as other unexpected components. Twelve grams of the resin were then loaded in an ion-exchange column (13 mm internal diameter and 200 mm length). Before use, the column was conditioned with 20 ml of 1.5 M HCl for Pb separation.

Methods

Leaching of ^{210}Pb and ^{210}Po from the air samples of glass-fiber filter: The air samples together with 25 mg Pb^{2+} carrier, 0.050 Bq of ^{209}Po tracer, 60 ml of conc. HNO_3 and 10 ml of conc. HCl were added to a 250 ml beaker, which were then heated at 240°C to leach the analytes for 30 min. The sample solution was evaporated to incipient dryness and 40 ml of 72% HClO_4 were added. The solution was evaporated to fuming to destroy all organic matters until a colourless residue was obtained. Three 6 ml portions of conc. HCl were consecutively added to change the solution medium and evaporated to dryness. The residue was finally dissolved with 20 ml of conc. HCl and some water. The obtained solution was filtered through a Millipore filter paper (pore size: $0.1 \mu\text{m}$; diameter: 47 mm) and collected in a 100 ml of tarred beaker. The quantity of the leaching solution was obtained by the gravimetric method.

Separation and determination of ^{210}Po : Twenty percent of the leaching solution obtained from Leaching of ^{210}Pb and ^{210}Po from the air samples of glass-fiber filter were put in a 100 ml beaker. Five ml of 20% hydroxylamine hydrochloride and 5 ml of 25% sodium citrate solution were added. The pH of the solution was adjusted to about 1.5 with 1:1 (v/v) ammonia. The solution was diluted to 50 ml, heated and stirred

Sample code	Aerodynamic diameter, μm	Sampling site	Sampling date	Sampling volume, m^3	Mass concentration of particle, $\mu\text{g m}^{-3}$	Latitude (N)	Longitude (E)
AP 7	≤ 2.5	Via Machiavelli, Taranto	11-11-2008	1621.36	19.16	$40^\circ 29' 18.76''$	$17^\circ 13' 33.47''$
AP 8	≤ 2.5	Via Machiavelli, Taranto	12-11-2008	1632.73	13.91	$40^\circ 29' 18.76''$	$17^\circ 13' 33.47''$
AP 9	≤ 2.5	Via Machiavelli, Taranto	13-11-2008	1338.25	4.73	$40^\circ 29' 18.76''$	$17^\circ 13' 33.47''$
AP 10	≤ 2.5	Cisi, Taranto	14-11-2008	1565.65	5.87	$40^\circ 29' 39.74''$	$17^\circ 13' 33.47''$
AP 11	≤ 2.5	Cisi, Taranto	15-11-2008	216.03	3.84	$40^\circ 29' 39.74''$	$17^\circ 13' 33.47''$
AP 12	≤ 2.5	Cisi, Taranto	16-11-2008	1606.58	5.03	$40^\circ 29' 39.74''$	$17^\circ 13' 33.47''$
AP 1	≤ 10	Via Machiavelli, Taranto	11-11-2008	1609.99	30.68	$40^\circ 29' 18.76''$	$17^\circ 13' 33.47''$
AP 2	≤ 10	Via Machiavelli, Taranto	12-11-2008	1608.85	22.01	$40^\circ 29' 18.76''$	$17^\circ 13' 33.47''$
AP 3	≤ 10	Via Machiavelli, Taranto	13-11-2008	1331.43	9.82	$40^\circ 29' 18.76''$	$17^\circ 13' 33.47''$
AP 4	≤ 10	Cisi, Taranto	14-11-2008	1586.11	14.86	$40^\circ 29' 39.74''$	$17^\circ 13' 33.47''$
AP 5	≤ 10	Cisi, Taranto	15-11-2008	204.66	21.47	$40^\circ 29' 39.74''$	$17^\circ 13' 33.47''$
AP 6	≤ 10	Cisi, Taranto	16-11-2008	1590.66	11.85	$40^\circ 29' 39.74''$	$17^\circ 13' 33.47''$
AP 13	≤ 10	Castel Romano (Roma)	19/29-11-2008	550.346	23.40	$41^\circ 42' 11.37''$	$12^\circ 26' 52.77''$

Table 1: Characteristics of the sampling sites for atmospheric particulate (AP) collected in the sampling campaign of Nov 2008 [the range (mean) mass concentration of particulate: $3.84 - 30.68$ (13.6 ± 8.4) $\mu\text{g m}^{-3}$].

Sample code	Aerodynamic diameter, μm	Sampling site	Sampling date	Sampling volume, m^3	Latitude (N)	Longitude (E)
AP14	≤ 2.5	Alto Adige, Taranto	4/5-5-2009	110.4	$40^\circ 27' 38.58''$	$17^\circ 15' 49.04''$
AP15	≤ 2.5	Alto Adige, Taranto	6/7-5-2009	110.4	$40^\circ 27' 38.58''$	$17^\circ 15' 49.04''$
AP16	≤ 2.5	Via Machiavelli, Taranto	4/5-5-2009	110.4	$40^\circ 29' 18.76''$	$17^\circ 13' 33.15''$
AP17	≤ 2.5	Via Machiavelli, Taranto	6/7-5-2009	110.4	$40^\circ 29' 18.76''$	$17^\circ 13' 33.15''$
AP18	≤ 10	Via delle Sorgenti, Statte	4/5-5-2009	110.4	$40^\circ 33' 44.95''$	$17^\circ 12' 12.33''$
AP19	≤ 10	Via delle Sorgenti, Statte	6/7-5-2009	110.4	$40^\circ 33' 44.95''$	$17^\circ 12' 12.33''$
AP20	≤ 10	Via delle Sorgenti, Statte	8/9-5-2009	110.4	$40^\circ 33' 44.95''$	$17^\circ 12' 12.33''$

Table 2: Characteristics of the sampling sites for atmospheric particulate (AP) collected in the sampling campaign of May 2009.

Sample No.	Sample weight, g	Pb yield, %	^{210}Pb , Bq kg $^{-1}$
IAEA-315-1	2.44	91.7	32.7 ± 1.4
IAEA-315-2	2.48	96.2	32.7 ± 1.4
IAEA-315-3	2.46	88.6	29.4 ± 1.3
IAEA-315-4	2.54	90.0	28.8 ± 1.3
IAEA-315-5	2.56	93.4	30.9 ± 1.3
IAEA-315-6	2.53	91.7	29.6 ± 1.3
Mean ± 1SD Range	2.44-2.48	91.9 ± 2.6 88.6-96.2	30.7 ± 1.7 28.8-32.7

*: The recommended value (95% confidence interval) of ^{210}Pb are 30.1 (26.0-33.7) Bq kg $^{-1}$.

Table 3: Experimental values of ^{210}Pb activity concentrations (corrected to the date of 1st Jan. 1993) in the IAEA-315 Marine Sediment.

on a hot-plate magnetic stirrer (10 min). A Perspex holder with a silver disk was placed on the beaker and the silver disk was immersed into the solution. Any air bubbles trapped beneath the disk were removed by manipulation of the stirrer bar. The polonium deposition was continued for 4 h at 85-90°C then the disk was removed, washed with distilled water and acetone, dried and assayed by alpha spectrometry [19].

Separation and determination of ^{210}Pb : Eighty percent of the leaching solution obtained from Leaching of ^{210}Pb and ^{210}Po from the air samples of glass-fiber filter were neutralized to pH 1.0 - 1.5 with ammonia solution, and 10-20 g of NH_4Ac were added and dissolved by heating. Four ml of 0.5 M Na_2S were added, and in this case PbS and FeS was precipitated while most of Ca^{2+} and Mg^{2+} will remain in the solution. The precipitates together with solution were transferred to a centrifuging tube and centrifuged at 4000 rpm for 5 min. After centrifugation, the supernatant was discarded and the black precipitate was dissolved with 3 ml of conc. HCl and 21 ml water. Digestion was made by adding 2 ml of 30% H_2O_2 , then the solution was filtered through a Millipore filter paper (pore size: 0.1 μm ; diameter: 47 mm).

The obtained solution was passed through a pre-conditioned anion-exchange resin column at room temperature and at a free flow rate. After washing with 40 ml of 1.5 M HCl, Pb was eluted with 60 ml of distilled water at free flow rate, and the separation time of the pair $^{210}\text{Pb}/^{210}\text{Bi}$ was recorded. Two ml of conc. H_2SO_4 were added to the collected eluant, which was then evaporated until fuming to destroy the organic matters by oxidation with 1 ml of 30% H_2O_2 . Both the precipitate and the solution were centrifuged. The supernatant was discarded and the precipitate was filtered on a weighed filter paper with a diameter of 24 mm (Whatman 42). The filter together with the precipitate was dried at 110°C until constant weight (about 1 h) and weighed again to calculate the lead chemical yield.

Lead-210 was determined by measuring the in-growth activity of its progeny ^{210}Bi ($T_{1/2}$: 120 h) by a low background β -counter sometime after separation (about one month being suitable). The ^{210}Pb activity concentration ($C_{\text{Pb-210}}$) in air sample (Bq m $^{-3}$) was calculated according to the following equation:

$$C_{\text{Pb-210}} = A_{\text{Bi-210}} / \left[\left(1 - e^{-\lambda_{\text{Bi-210}} t} \right) \eta Y V \right] \quad (1)$$

where, $A_{\text{Bi-210}}$ is the net count rate of ^{210}Bi (cps); λ_{Bi} , the ^{210}Bi decay constant (min $^{-1}$); t , the ^{210}Bi in-growth time after ^{210}Pb separation (min); η , the detection efficiency for ^{210}Bi ; Y , the chemical yield; and V , the sampling volume (m 3) for air.

Quality control: Following approaches can be used to review the quality of a radio analytical method: (1) to analyze the certified reference materials or similar matrices and to compare the obtained results with the recommended values, and (2) to participate in the inter-comparison activities between different international laboratories.

For the purpose of quality control, the reference material IAEA-315 Marine Sediment supplied by the IAEA was used. About 2 g of the reference material were analyzed following the recommended procedure of this paper. The precision was evaluated by the relative standard deviation obtained from a set of six analyses. The accuracy was assessed by the term of relative bias, which reflects the difference between the experimental mean and recommended value of ^{210}Pb activity concentration. Due to the presence of unsupported ^{210}Pb in the IAEA-315, the fraction of unsupported ^{210}Pb had to be corrected to the base date.

The obtained ^{210}Pb activity concentrations in the IAEA-315 were shown in Table 3. The mean ^{210}Pb concentration in the IAEA-315 was found to be 30.7 ± 1.7 Bq kg $^{-1}$ (decay correction to the date of 1st Jan. 1993). It was observed that the relative standard deviation is ± 5.5% for ^{210}Pb . Since all being less than ± 10% the precision for the analyses is well acceptable as far as such a low activity is concerned. The relative bias obtained from the analyses was +2.0% for ^{210}Pb , showing that the mean activity concentration of ^{210}Pb is in good agreement with the recommended value of 30.1 Bq kg $^{-1}$ (the 95% confidence interval: 26.0-33.7 Bq kg $^{-1}$).

Due to its short half-life, the reference materials for ^{210}Po are not available. The quality control for ^{210}Po analyses in this laboratory was carried out through participating in the intercomparison activities organized by the IAEA in 29 March 2007. The samples for intercomparison were a set of five water samples. The obtained activity concentrations of ^{210}Po were all in good agreement with the values given by the IAEA.

Detection limits: Taking into account the 3 σ of the blank count rates, the counting efficiencies of the instrument, the radiochemical yields, the in-growth or decay factor (^{210}Pb : 100%) and the sampling volume, the detection limit, or more precisely, the minimum detectable activity (MDA) of the method for air samples was 1.7 $\mu\text{Bq m}^{-3}$ for both ^{210}Po and ^{210}Pb .

Results and Discussion

^{210}Po and ^{210}Pb concentrations in atmospheric particles:

The atmospheric particulate masses of ≤ 2.5 μm in an aerodynamic diameter are considered as the most harmful particles from health physics point of view, as they can be easily inhaled and dissolved in lung. Two kinds of atmospheric particulate samples were taken, one with a atmospheric particulate mass concentration in the fraction of an aerodynamic diameter ≤ 2.5 μm ($\text{PM}_{2.5}$), and another in the fraction of ≤ 10 μm (PM_{10}). The uncorrected ^{210}Po and ^{210}Pb concentrations in $\mu\text{Bq m}^{-3}$ in atmospheric particulate collected in 11-29 Nov. 2008 at the site Taranto (AP 1-12) and CSM Roma (AP13) and analyzed in 9-19 Dec. 2008 were reported in Table 4 (the first sampling campaign), and that collected at site Taranto (AP 14-20) in 4-9 May 2009 and analyzed in

Sample code	Sampling site	Aerodynamic diameter, μm	Po yield, %	²¹⁰ Po	Pb yield, %	²¹⁰ Pb	²¹⁰ Po/ ²¹⁰ Pb
AP7	Via Machiavelli	≤ 2.5	92.5	130 ± 6	84.5	975 ± 41	0.133
AP8	Via Machiavelli	≤ 2.5	96.9	214 ± 9	85.2	1054 ± 45	0.203
AP9	Via Machiavelli	≤ 2.5	90.2	83.5 ± 4.2	91.0	362 ± 15	0.231
AP10	Cisi	≤ 2.5	99.8	75.0 ± 3.7	90.0	464 ± 20	0.162
AP11	Cisi	≤ 2.5	96.6	65.9 ± 6.8	90.3	444 ± 20	0.148
AP12	Cisi	≤ 2.5	96.7	45.8 ± 2.7	82.8	298 ± 13	0.154
AP1	Via Machiavelli	≤ 10	91.2	131 ± 7	94.8	1083 ± 46	0.121
AP2	Via Machiavelli	≤ 10	96.2	226 ± 11	91.4	1099 ± 46	0.206
AP3	Via Machiavelli	≤ 10	100.0	77.9 ± 3.8	95.8	358 ± 15	0.217
AP4	Cisi	≤ 10	93.0	81.5 ± 3.9	91.4	484 ± 21	0.169
AP5	Cisi	≤ 10	91.6	77.2 ± 7.5	90.3	520 ± 23	0.149
AP6	Cisi	≤ 10	100.1	43.1 ± 2.0	87.2	331 ± 14	0.130
AP13	CSM Roma	≤ 10	93.1	48.5 ± 3.3	84.2	399 ± 17	0.122
Mean ± 1SD	-	-	95.2 ± 3.5	100 ± 60	89.1 ± 4.1	605 ± 318	0.165 ± 0.038
Range	-	-	90.2-100.1	43.1-226	82.8-95.8	298-1099	0.121-0.231

Table 4: The ²¹⁰Po and ²¹⁰Pb activity concentrations in μBq m⁻³ in atmospheric particulate samples AP 1-12 collected at Taranto in 11-17 Nov. 2008 and AP 13 at CSM Roma in 19-29 Nov. 2008 and calculated at the determination time of 9-19 Dec. 2008.

Sample code	Sampling site	Aerodynamic diameter, μm	Po yield, %	²¹⁰ Po	Pb yield, %	²¹⁰ Pb	²¹⁰ Po/ ²¹⁰ Pb
AP14	Alto Adige	≤ 2.5	100.3	246 ± 15	95.5	707 ± 31	0.348
AP15	Alto Adige	≤ 2.5	86.2	221 ± 13	100	664 ± 29	0.333
AP16	Via Machiavelli	≤ 2.5	100	218 ± 12	100	610 ± 27	0.357
AP17	Via Machiavelli	≤ 2.5	71.9	154 ± 11	100.3	641 ± 28	0.240
AP18	Via delle Sorgenti, Statte	≤ 10	88.5	193 ± 12	95.1	627 ± 27	0.308
AP19	Via delle Sorgenti, Statte	≤ 10	96.9	171 ± 13	91.0	716 ± 31	0.239
AP20	Via delle Sorgenti, Statte	≤ 10	90.8	265 ± 16	100.9	955 ± 41	0.277
Mean ± 1SD	-	-	90.7 ± 10.0	210 ± 40	97.5 ± 3.7	754 ± 118	0.300 ± 0.049
Range	-	-	71.9-100.3	154-265	91.0-100.9	610-955	0.239-0.357

Table 5: The ²¹⁰Po and ²¹⁰Pb activity concentrations in μBq m⁻³ in atmospheric particulate samples collected at Taranto in 4-9 May 2009 and calculated at the determination time of 24-26 June 2009.

24-26 June 2009 were given in Table 5 (the second sampling campaign) [20].

As the sampling sites are far from the laboratory and the sample analyses were done with a delay of some days, consequently, the activity concentrations of ²¹⁰Pb in air in Tables 4 and 5 were underestimated due to the ²¹⁰Pb decay, and the activity concentrations of ²¹⁰Po were overestimated due to its in-situ production from ²¹⁰Pb-²¹⁰Bi decay. Therefore, the activity concentrations of ²¹⁰Pb and ²¹⁰Po given in Tables 4 and 5 were corrected to the sampling time.

The activity concentrations of ²¹⁰Pb at sampling time (A_{Pb210}) were corrected by equation 2:

$$A_{Pb210} = A_{Pb210}^t / e^{-\lambda_{Pb-210}t} \quad (2)$$

where, A_{Pb210}^t was obtained at the ²¹⁰Pb determination time (Tables 4 and 5); λ_{Pb210} , the ²¹⁰Pb decay constant; t , the time from air sampling to analyzing.

The ²¹⁰Po activity concentration (A_{Po210}^i) produced from ²¹⁰Pb (A_{Pb210}) decay through ²¹⁰Bi at the sample determination time (t) can be calculated from equation 3, which was derived from Bateman's equation [21]:

$$\frac{A_{Po210}^i}{A_{Pb210}} = \lambda_{Po210} A_{Pb210} \left[\frac{e^{-\lambda_{Po210}t}}{(\lambda_{Bi210} - \lambda_{Po210})(\lambda_{Pb210} - \lambda_{Po210})} + \frac{e^{-\lambda_{Bi210}t}}{(\lambda_{Pb210} - \lambda_{Bi210})(\lambda_{Pb210} - \lambda_{Po210})} + \frac{e^{-\lambda_{Pb210}t}}{(\lambda_{Bi210} - \lambda_{Pb210})(\lambda_{Pb210} - \lambda_{Po210})} \right] \quad (3)$$

where, A_{Pb210} can be obtained from equation 2. In the bracket of equation 3, the first and second terms describe the ²¹⁰Po fraction derived from ²¹⁰Pb and ²¹⁰Bi, and the last term the fraction of ²¹⁰Po decayed. Therefore, the ²¹⁰Po activity concentration (A_{Po210}^i Bq m⁻³) present at the sampling time can be obtained from:

$$A_{Po210} = (A_{Po210}^i - A_{Po210}^t) / e^{-\lambda_{Po210}t} \quad (4)$$

where, A_{Po210}^t was the activity concentrations of ²¹⁰Po at the determination time given in Tables 4 and 5.

The corrected activity concentrations of ²¹⁰Pb and ²¹⁰Po in sampling time were reported in Tables 6 and 7. It was indicated that in the first sampling campaign (Table 6) the obtained ²¹⁰Po activity concentrations in samples of PM_{2.5} and PM₁₀ were in the range of 11.9–112 (mean: 37.5 ± 38.0) μBq m⁻³ and 13.3–99.8 (37.0 ± 30.4) μBq m⁻³, that of ²¹⁰Pb in the range of 300–1060 (603 ± 330) μBq m⁻³ and 333–1105 (614 ± 337) μBq m⁻³, and the ²¹⁰Po/²¹⁰Pb activity concentration ratios in the range of 0.0273–0.113 (0.0596 ± 0.0389) and 0.0274–0.1247 (0.0620 ± 0.0376), respectively.

At first glance of the data in Table 6 and the weather record, the activity concentrations of ²¹⁰Po and ²¹⁰Pb were highly variable, in particular, depending on the variability of weather conditions encountered during the sampling period. During rain events less particulate matter was collected, and thus, also lower activity concentrations of ²¹⁰Po and ²¹⁰Pb were detected. The second characteristic of the data in Table 6 was the great difference between the ²¹⁰Pb and ²¹⁰Po activity concentrations. Removal of ²¹⁰Pb and ²¹⁰Po from the atmosphere occurs mainly by wet and dry deposition of the carrier aerosol and their radioactive decay. Since the residence times of the atmospheric aerosols are much shorter than the half-life of the ²¹⁰Po progeny, this species cannot reach secular equilibrium with its predecessors. Therefore, ²¹⁰Po atmospheric concentration is much lower than that of ²¹⁰Pb and the average concentrations of ²¹⁰Po in surface air were observed to be 6.3 ± 3.7% of that of ²¹⁰Pb in the region of South Italy.

Sample code	Sampling site	Aerodynamic diameter, μm	^{210}Po	^{210}Pb	$^{210}\text{Po}/^{210}\text{Pb}$	Residence time, d
AP7	Via Machiavelli	≤ 2.5	26.7 ± 1.6	981 ± 42	0.0273	9.89
AP8	Via Machiavelli	≤ 2.5	112 ± 7	1060 ± 45	0.1055	30.1
AP9	Via Machiavelli	≤ 2.5	41.0 ± 2.7	364 ± 15	0.1128	32.0
AP10	Cisi	≤ 2.5	20.3 ± 1.3	467 ± 20	0.0434	14.0
AP11	Cisi	≤ 2.5	13.0 ± 1.5	447 ± 20	0.0291	10.4
AP12	Cisi	≤ 2.5	11.9 ± 0.9	300 ± 13	0.0398	13.1
AP1	Via Machiavelli	≤ 10	29.8 ± 2.0	1089 ± 46	0.0274	9.93
AP2	Via Machiavelli	≤ 10	99.8 ± 6.5	1105 ± 47	0.0903	26.0
AP3	Via Machiavelli	≤ 10	44.9 ± 2.9	360 ± 15	0.1247	35.3
AP4	Cisi	≤ 10	40.0 ± 2.5	486 ± 21	0.0823	24.0
AP5	Cisi	≤ 10	15.4 ± 1.6	523 ± 23	0.0295	10.5
AP6	Cisi	≤ 10	15.5 ± 1.0	333 ± 14	0.0466	14.9
AP13	CSM Roma	≤ 10	13.3 ± 1.1	401 ± 17	0.0331	11.4
Mean \pm 1SD	-	-	39.2 ± 33.2	626 ± 327	0.0632 ± 0.0372	19.2 ± 9.6
Range	-	-	11.9-112	300-1105	0.0273-0.1247	9.89-35.3

Table 6: The ^{210}Po and ^{210}Pb activity concentrations in $\mu\text{Bq m}^{-3}$ in atmospheric particulate samples AP 1-12 collected at Taranto in 11-17 Nov. 2008 and AP 13 at CSM Roma in 19-29 Nov. 2008 and corrected to the sampling time and the calculated residence times.

Sample code	Sampling site	Aerodynamic diameter, μm	^{210}Po	^{210}Pb	$^{210}\text{Po}/^{210}\text{Pb}$	Residence time, d
AP14	Alto Adige	≤ 2.5	122 ± 9	727 ± 31	0.168	47.9
AP15	Alto Adige	≤ 2.5	106 ± 8	683 ± 30	0.155	44.1
AP16	Via Machiavelli	≤ 2.5	109 ± 8	627 ± 28	0.174	49.7
AP17	Via Machiavelli	≤ 2.5	34.2 ± 2.8	659 ± 29	0.0519	16.2
AP18	Via delle Sorgenti, Statte	≤ 10	72.8 ± 5.6	644 ± 28	0.113	32.1
AP19	Via delle Sorgenti, Statte	≤ 10	37.1 ± 3.3	736 ± 32	0.0504	15.8
AP20	Via delle Sorgenti, Statte	≤ 10	102 ± 8	982 ± 42	0.104	29.7
Mean \pm 1SD	-	-	83.4 ± 35.8	722 ± 121	0.117 ± 0.052	33.6 ± 14.2
Range	-	-	34.2-122	627-982	0.0504-0.174	15.8-49.7

Table 7: The ^{210}Po and ^{210}Pb activity concentrations in $\mu\text{Bq m}^{-3}$ in atmospheric particulate samples collected at Taranto in 4-9 May 2009 and corrected to the sampling time and the calculated residence times.

In the UNSCEAR reports [22] the reference concentrations in air were about $50 \mu\text{Bq m}^{-3}$ (ranged from 12 to $80 \mu\text{Bq m}^{-3}$) for ^{210}Po and $500 \mu\text{Bq m}^{-3}$ (ranged from 28 to $2250 \mu\text{Bq m}^{-3}$) for ^{210}Pb , respectively, and they were site specific. It was reported that the yearly average concentrations of ^{210}Pb in surface air over Europe were about 200-700 $\mu\text{Bq m}^{-3}$. Therefore, the obtained concentrations of ^{210}Po and ^{210}Pb in this study should be well in agreement with the reported values.

Lead-210 and ^{210}Po in atmosphere comes from several sources: (1) from volcanic dust [23,24], (2) from resuspended soil particles [25], (3) from ^{222}Rn gas which is emitted from the ground into the atmosphere [10,17], and (4) from fossil fuel combustion, biomass burning and industrial processes including mining and smelting of uranium, phosphate, lead and iron ore [17,26]. The first three categories are natural sources, while the fourth is anthropogenic.

The contribution of ^{210}Pb and ^{210}Po in air from the first category source is negligible in this study, as there were no any volcanic eruptions in the surrounding region during the investigation period. The contribution from the second category source is also negligible, as it is usual that the ^{210}Po and ^{210}Pb activities in the resuspended soil particles in air should be in equilibrium (i.e. ratio is about 1.0), and in these measurements the $^{210}\text{Po}/^{210}\text{Pb}$ ratios were well below that value. The contribution from the fourth category source cannot be excluded, but it seems less important if compared with that in the control site (AP13) in most days of the sampling. In fact, the ^{222}Rn gas exhalation from the ground into the atmosphere (the third category) is the most important source contribution of ^{210}Po and ^{210}Pb in the obtained samples. As shown in Table 6, at the same site the activity concentrations of ^{210}Po and ^{210}Pb found in the sample category of PM_{10} did not differ from the corresponding values found in the sample category of $\text{PM}_{2.5}$, thus it

was showed that almost all of ^{210}Po and ^{210}Pb were found only in the atmospheric particulate fraction with aerodynamic diameters $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$), and this conclusion is consistent with that reported by Marley et al. [11]. Studies showed that, when inhaled, smaller particles can be more toxic than a comparable mass of larger particles of the same material, as the health effects are directly linked to their bigger particle surface area and higher solubility [27].

The second sampling campaign for atmospheric particle samples was carried out at 4 sites in Taranto in 4-9 May 2009. As shown in Table 7, the corrected ^{210}Po activity concentrations in the samples of $\text{PM}_{2.5}$ and PM_{10} were in the range of 34.2-122 (mean: 92.8 ± 39.7) $\mu\text{Bq m}^{-3}$ and 37.1-102 (70.6 ± 32.5) $\mu\text{Bq m}^{-3}$, that of ^{210}Pb in the range of 627-727 (674 ± 42) $\mu\text{Bq m}^{-3}$ and 644-982 (787 ± 175) $\mu\text{Bq m}^{-3}$, and the $^{210}\text{Po}/^{210}\text{Pb}$ activity concentration ratios in the range of 0.0519-0.174 (0.137 ± 0.057) and 0.0504-0.113 (0.0891 ± 0.0338), respectively. Compared with the results in Table 6 (the first sampling campaign), the concentrations of ^{210}Pb (Table 7) in the samples of the second sampling campaign seem unchanged, while that of ^{210}Po were doubled. The $^{210}\text{Po}/^{210}\text{Pb}$ ratio variation could be a characteristic of the seasonal variation of ^{210}Po and ^{210}Pb in the atmosphere of the region.

The atmospheric residence time of aerosol in the studied region

In this work ^{210}Po and ^{210}Pb were used as the atmospheric tracers, and the residence times of aerosol in the region of South Italy were calculated based on the activity concentration ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in the atmospheric particles.

Theoretical basis for calculation of the atmospheric residence

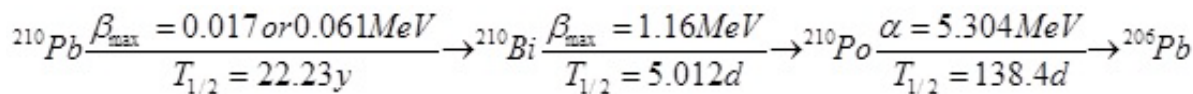


Figure 1: The decay chain of ^{210}Pb .

time of aerosol: Lead-210 is the progeny of ^{222}Rn . The main decay chain of ^{210}Pb is shown in Figure 1.

Lead-210, ^{210}Bi and ^{210}Po , all are particle-reactive and can be rapidly adsorbed to atmosphere aerosol after they are produced with average attachment time of 40 s to 3 min [28]. If all ^{210}Pb in the sampling site is produced from the decay of ^{222}Rn in the air and all ^{210}Po is derived from ^{210}Pb (i.e. no additional source of ^{210}Po and ^{210}Pb), then using a simple steady-state model, the disequilibrium between ^{210}Po and ^{210}Pb can be utilized to determine the residence time of the aerosols. In a well-mixed, isolated atmospheric sample where the rate of supply of radon gas is constant, the rate of change of decay product concentration with the elapsed time (t) can be expressed as a differential equation [4,6,29,30]:

$$dN_d / dt = \lambda_p N_p - (\lambda_d + \lambda_r) N_d \quad (5)$$

where N_p and N_d are the atom concentrations of parent and daughter products; λ_p and λ_d , their respective decay constant (reciprocal lifetime); λ_r , the removal rate constant of aerosol. Under equilibrium conditions,

$$N_d \lambda_d / \lambda_p N_p = \lambda_d (\lambda_d + \lambda_r) \quad (6)$$

In case where the activity concentration ratios of products are separated by an intermediate decay product, such as the ratio of ^{210}Po to ^{210}Pb via ^{210}Bi , the ratio was given by Robbins [31]:

$$N_{Po210} \lambda_{Po210} / N_{Pb210} \lambda_{Pb210} = \lambda_{Po210} \lambda_{Bi210} / [(\lambda_{Bi210} + \lambda_r)(\lambda_{Po210} + \lambda_r)] \quad (7)$$

or

$$A_{Po210} / A_{Pb210} = \lambda_{Po210} \lambda_{Bi210} / [(\lambda_{Bi210} + \lambda_r)(\lambda_{Po210} + \lambda_r)] \quad (8)$$

where, A_{Po210} and A_{Pb210} is the respective activity concentration (Bq m^{-3}) of ^{210}Po and ^{210}Pb in air; λ_{Pb210} ($0.00008537 \text{ d}^{-1}$), λ_{Bi210} (0.1383 d^{-1}), and λ_{Po210} (0.002009 d^{-1}), the decay constant of ^{210}Pb , ^{210}Bi and ^{210}Po , respectively.

The residence time of atmospheric aerosols in days, T_r , was defined as the reciprocal of the removal rate constant of aerosol, i.e., $T_r = 1/\lambda_r$, therefore,

$$A_{Po210} / A_{Pb210} = T_r^2 / (T_r + 1/\lambda_{Bi210}) \times (T_r + 1/\lambda_{Po210}) \quad (9)$$

Since the ratio of A_{Po210}/A_{Pb210} increases exponentially with time, a value of the mean tropospheric or atmospheric residence time of the associated aerosols can be calculated from equation 9.

The atmospheric residence times of aerosol in the region of South Italy: The calculated residence times of aerosol in the region of South Italy based on the activity concentration ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in the atmospheric particles and on the equation 9 were also given in Tables 6 and 7. It was summarized that the calculated residence times of aerosol collected in the first sampling campaign were ranged from 8.89 to 35.3 days with a mean value of 19.2 ± 9.6 days, and that in the second sampling campaign from 15.8 to 49.7 days with a mean value of 33.6 ± 14.2 days. The residence times were not classified as the particulate size, as the residence times as a function of the particulate size were not observable. The variations of the residence time observed in the two sampling campaigns could be a reflection of the seasonal variations.

Discussion about the residence times of aerosol obtained from different techniques and regions: Martell and Moore [10,14] discussed the available evidence concerning tropospheric aerosol removal rates and concluded that residence times in the troposphere are 1 week or less. After literature investigation, the residence times obtained from different techniques and regions were summarized in Table 8. It was shown that the residence times are extremely variable, as they are dependent on the sources, meteorology, composition, transport and mixing, as well as wet and dry removal rates of the associated aerosols to which the radionuclides are attached. In fact, the removal of particulate matter is primarily by precipitation scavenging, and this suggests that seasonal variation of the precipitation should contribute to seasonal fluctuations of tracer concentrations in surface air. This effect should be in addition to those of seasonal transport within the stratosphere and seasonal changes of stratosphere mass. It was Hvinden et al. [32] that first recognized the important effect of precipitation rate on seasonal and latitudinal variations of radioactive fallout.

It was considered that the concept of a single residence time for the whole troposphere is not valid, as it consists of different layers like the planetary boundary layer, the middle and upper troposphere, the polar atmosphere etc., with different scavenging and mixing properties [33]. The value of residence time obtained with the various radioactive tracers will therefore refer to their mean production levels, e.g., ^7Be , ^{32}P , for upper troposphere, and ^{210}Pb , ^{210}Bi , ^{210}Po for the planetary boundary layer, etc. [34].

As shown in first 4 lines in Table 8, the residence times of atmospheric particles, which were associated with ^7Be -aerosol, vary from 2.6 – 35.4 days. Among the data, Shapiro and Forbes-Resha [35] estimated a mean atmospheric aerosol residence time of 35.4 days in two year measurements at Fullerton, California USA, while Winkler et al. [36] estimated the residence times of 5-6 days in 46 measurements sampled during >1 year period in ground level air at Neuherberg, Germany, being 6-times difference with the data of Shapiro and Forbes-Resha [35].

As shown in Table 8, the $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{35}\text{S}$ ratios in air has been used to estimate the tropospheric residence times, and the obtained mean tropospheric residence time was 44.1 and 42.8 days, respectively. Due to the numerous sampling numbers, it seems less variations of the mean residence time were observed. However, the comparison of ^7Be with ^{137}Cs of stratospheric origin in surface air indicated the presence of a stratospheric component of ^7Be [37,38], the magnitude of which is varying and time dependent. Hence the tropospheric residence times calculated from the $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{35}\text{S}$ ratios are less reliable. The same disputes or even worse reputation also happened to $^7\text{Be}/^{22}\text{Na}$ ratios.

Strontium-90 has also been used for atmospheric studies; however, there are few data available for estimation of the residence times in our collected literatures.

Radon-222 is a short-life, inert gaseous and natural occurring radionuclide. In an ideal enclosed air mass (closed system with respect to these nuclides), the residence times of aerosols obtained from the activity ratios of $^{210}\text{Pb}/^{222}\text{Rn}$, $^{210}\text{Bi}/^{210}\text{Pb}$, and $^{210}\text{Po}/^{210}\text{Pb}$ are expected

Method No.	Regions studied	Sampling time	Latitude-Longitude	Aerodynamic diameter, μm	Tracer used	Sample numbers	Range of the ART, days	Mean of the ART, days	References
1	Thessaloniki Greece	Nov. 2006-June 2008	40.63°N-22.97°E	0.76-1.18	^7Be	12	7.4 - 8.9	8.0	[5]
2	Neuherberg Gemany	1996-1997	48.22°N-11.60°E	-	^7Be	46	5 - 6	-	[36]
3	Fullerton USA	1974-1975	33.87°N-117.92°W	-	^7Be	-	-	35.4	[35]
4	Hongkong China	Nov.-March 2001	22.30°N-114.17°E	-	^7Be	-	2.6 -11.8	-	[11]
5	Leningrad USSR	1963-1966	59.92°N-30.33°E	-	$^7\text{Be}/^{32}\text{P}$	117	10 - 100	42 \pm 15	[41]
6	Berne Austria	1965	51.78°N-11.73°E	-	$^7\text{Be}/^{32}\text{P}$	19	20 - 60	41 \pm 9	[42]
7	Toulouse France	1967	43.62°N-1.45°E	-	$^7\text{Be}/^{32}\text{P}$	120	15 - 75	30 \pm 10	[15]
8	Vilnius USSR	1967-1969	54.63°N-25.32°E	-	$^7\text{Be}/^{32}\text{P}$	24	8 - 47	26 \pm 9.3	[43]
9	Bavarian Alps Austria	1970-1980	48.83°N-12°E	-	$^7\text{Be}/^{32}\text{P}$	3000	20 - 60	34 \pm 17	[44]
10	Antarctic Cont.	1977-1981	-	-	$^7\text{Be}/^{32}\text{P}$	26	46 - 132	73 \pm 29	[45]
11	Troposphere	1959-1965	10 - 70°N	-	$^7\text{Be}/^{32}\text{P}$	17	22 - 71	43 \pm 16	[46]
12	Stratosphere	1959-1965	10 - 70°N	-	$^7\text{Be}/^{32}\text{P}$	21	47 - 93	64 \pm 14	[46]
13	Leningrad USSR	1964-1966	59.92°N-30.33°E	-	$^7\text{Be}/^{35}\text{S}$	86	5 - 70	23 \pm 7.3	[41]
14	Aspendale Australia	1967-1968	37.83°S-145°E	-	$^7\text{Be}/^{35}\text{S}$	8	30 - 150	78 \pm 38	[47]
15	Bavarian Alps Austria	1973-1975	48.83°N-12°E	-	$^7\text{Be}/^{35}\text{S}$	600	10 - 60	31 \pm 10	[48]
16	Upper atmosphere	1960-1961	-	-	$^7\text{Be}/^{35}\text{S}$	17	17 - 68	39 \pm 10.5	[49]
17	Vilnius USSR	1965-1969	54.63°N-25.32°E	-	$^7\text{Be}/^{22}\text{Na}$	48	530 - 19000	4400 \pm 4400	[43]
18	Richland USA	1968-1976	43.35°N-90.38°W	-	$^7\text{Be}/^{22}\text{Na}$	100	-	3000	[49]
19	Troposphere	1960-1961	-	-	$^7\text{Be}/^{22}\text{Na}$	12	2630 - 14280	7200 \pm 3300	[50]
20	Stratosphere	1960-1961	-	-	$^7\text{Be}/^{22}\text{Na}$	15	1550 - 11110	4500 \pm 2400	[50]
21	BalboaGemany/USA	Feb. 1963	-	-	^{90}Sr	-	<3d – months	-	[51,52]
22	ANL USA	June-July 1998	41.7°N-88.0°W	0.1-10	$^{210}\text{Bi}/^{210}\text{Pb}$	7	6 - 67	37.7 \pm 19.1	[11]
23	PHX USA	May-June 1998	34.1°N-106.8°W	0.1-10	$^{210}\text{Bi}/^{210}\text{Pb}$	9	5 -78	43.7 \pm 20.3	[11]
24	NM USA	May 1998	33.5°N-111.8°W	0.1-10	$^{210}\text{Bi}/^{210}\text{Pb}$	4	41 - 63	50.3 \pm 9.4	[11]
25	Poker Flat USA	Jan.-Feb. 1996	65.1°N-147.5°W	-	$^{210}\text{Po}/^{210}\text{Pb}$	2	11.9 - 32	22 \pm 14	[4]
26	Eagle USA	March 1996	65.9°N-141.2°W	-	$^{210}\text{Po}/^{210}\text{Pb}$	6	9.5 – 38.7	23 \pm 11	[4]
27	ANL USA	June-August 1996	41.7°N-88.0°W	0.1-10	$^{210}\text{Po}/^{210}\text{Pb}$	19	27 - 66	44.4 \pm 10.6	[11]
28	ANL USA	June-July 1998	41.7°N-88.0°W	0.1-10	$^{210}\text{Po}/^{210}\text{Pb}$	7	24 - 71	41.4 \pm 15.0	[11]
29	PHX USA	May-June 1998	34.1°N-106.8°W	0.1-10	$^{210}\text{Po}/^{210}\text{Pb}$	10	16 - 73	47.1 \pm 17.8	[11]
30	NM USA	May 1998	33.5°N-111.8°W	0.1-10	$^{210}\text{Po}/^{210}\text{Pb}$	4	44 - 61	51.0 \pm 8.4	[11]
31	MC Mexico	Feb.-march 1997	19.5°N-99.0°W	0.1-10	$^{210}\text{Po}/^{210}\text{Pb}$	20	8 - 77	43.6 \pm 16.0	[11]
32	Taranto Italy	11-17 Nov. 2008	40.49°N-17.20°E	<2.5-10	$^{210}\text{Po}/^{210}\text{Pb}$	13	9.89 - 35.3	19.2 \pm 9.6	This work
33	Taranto Italy	4-9 May 2009	40.49°N-17.20°E	<2.5-10	$^{210}\text{Po}/^{210}\text{Pb}$	7	15.8 - 49.7	33.6 \pm 14.2	This work

Table 8: The atmospheric residence times (ART) of aerosol obtained from different techniques and regions.

to agree with each other. But a large number of studies have also indicated discordance between the residence times obtained from these three pairs. The discrepancies are due to deviations from these ideal conditions. Each method has its own advantages and disadvantages. For instance, the advantages of $^{210}\text{Bi}/^{210}\text{Pb}$ method are that the mean life of ^{210}Bi (7.2 d) is comparable to the mean residence time of aerosols and water vapor in the lower atmosphere and is less sensitive to extraneous sources than is $^{210}\text{Po}/^{210}\text{Pb}$ method, and the disadvantage is the time sensitive nature of this pair [39]. Therefore, it has been well-documented that the $^{210}\text{Bi}/^{210}\text{Pb}$ -based residence time is always lower than the $^{210}\text{Po}/^{210}\text{Pb}$ -based residence times. The advantages of $^{210}\text{Po}/^{210}\text{Pb}$ method are less time sensitive and the measurement techniques are more reliable, and the disadvantage is that volatile nature of ^{210}Po could result in additional sources of ^{210}Po to the atmosphere which could alter the residence time based on $^{210}\text{Po}/^{210}\text{Pb}$ pair (such as large amounts of ^{210}Po are released to the atmosphere from major volcanic events) [24,40]. Moreover, both methods could be affected by finite amount of resuspended dust or soil which will have higher $^{210}\text{Bi}/^{210}\text{Pb}$ and/or $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio in surface air sampling. Recent results from the distribution of these nuclides in size-fractionated aerosols appear to yield consistent residence time in smaller-size aerosols, possibly suggesting that the residence time discrepancies in larger size aerosols are derived from resuspended dust. Therefore, if applied properly, ^{222}Rn and its progeny products could be considered as the ideal tracers for

atmospheric studies, as vertical distribution profiles showed a more even distribution throughout the troposphere and stratosphere for their concentrations than for other atmospheric radionuclides [16]. As shown in Table 8, the mean values of the atmospheric residence times, estimated from the $^{210}\text{Bi}/^{210}\text{Pb}$ and $^{210}\text{Po}/^{210}\text{Pb}$ activity concentration ratios in the collected literatures, were 43.9 and 35.2 days, respectively.

Due to the fact in Table 6 that (1) the ^{210}Po or ^{210}Pb activity concentrations in samples of $\text{PM}_{2.5}$ and PM_{10} at the same site are nearly in the same level, and (2) the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios are much less than 1, it is judged that the particulate size in the collected samples is $\leq 2.5 \mu\text{m}$ and the contribution from resuspended soil in the samples is negligible. Therefore, the calculated atmospheric residence times of aerosol in South Italy, being 8.89-35.3 (mean: 19.2 \pm 9.6) days in the first sampling campaign and 15.8-49.7 (mean: 33.6 \pm 14.2) days in the second sampling campaign, were real reflection of the atmosphere transport characteristics or behaviours of the inorganic and organic atmosphere pollutants in the region of the Mediterranean Sea.

Conclusion

Based on the $^{210}\text{Po}/^{210}\text{Pb}$ activity concentration ratios, the estimated atmospheric residence times of aerosol in the region of South Italy were ranged from 8.89 to 35.3 days with a mean value of 19.2 \pm 9.6 days in the first sampling campaign in Nov 2008 and from 15.8 to 49.7

days with a mean value of 33.6 ± 14.2 days in the second sampling campaign in May 2009. After comparison with the data in literatures, it is concluded that the technique used in the study is reliable. The calculated atmospheric residence times of aerosol in South Italy, were real reflection of the atmosphere transport characteristics or behaviors of the inorganic and organic atmosphere pollutants in the region of the South Mediterranean Sea.

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