# **Atmospheric residence time of 210Pb determined from the activity ratios with its daughter radionuclides 210Bi and 210Po**

**Abstract**. The residence time of 210Pb created in the atmosphere by the decay of gaseous 222Rn is a key parameter controlling its distribution and fallout onto the landscape. These in turn are key parameters governing the use of this natural radionuclide for dating and interpreting environmental records stored in natural archives such as lake sediments. One of the principal methods for estimating the atmospheric residence time is through measurements of the activities of the daughter radionuclides 210Bi and 210Po, and in particular the 210Bi/210Pb and 210Po/210Pb activity ratios. Calculations used in early empirical studies assumed that these were governed by a simple series of equilibrium equations. This approach does however have two failings; it takes no account of the effect of global circulation on spatial variations in the activity ratios, and no allowance is made for the impact of transport processes across the tropopause. This paper presents a simple model for calculating the distributions of 210Pb, 210Bi and 210Po at northern mid-latitudes (30o−65oN), a region containing almost all the available empirical data. By comparing modelled 210Bi/210Pb activity ratios with empirical data a best estimate for the tropospheric residence time of around 10 days is obtained. This is significantly longer than earlier estimates of between 4−7 days. The process whereby 210Pb is transported into the stratosphere when tropospheric concentrations are high and returned from it when they are low, significantly increases the effective residence time in the atmosphere as a whole. The effect of this is to significantly enhance the long range transport of 210Pb from its source locations. The impact is illustrated by calculations showing the distribution of 210Pb fallout versus longitude at northern mid-latitudes.

**1. Introduction**

The natural radionuclide 210Pb is widely used for dating and interpreting environmental records stored in natural archives such as lake or marine sediments and peat bogs. Since the source of the 210Pb is atmospheric fallout, models of the processes controlling its distribution in the atmosphere and subsequent deposition onto the Earth’s surface are of considerable importance to this work. Outputs from the atmospheric model become inputs to models of the transport processes by which fallout deposited on the landscape accumulates in the sediment record. These terrestrial and aquatic models are of fundamental importance to the 210Pb dating methodology. They are also essential to the use of sediment records for reconstructing historical levels of atmospheric pollution by e.g. heavy metals (lead and mercury) and persistent organic pollutants (POPs). Use of 210Pb as a tracer for establishing the validity of these models requires good estimates of the atmospheric 210Pb flux. Good estimates of the 210Pb flux are also necessary to a reliable interpretation of 210Pb dating calculations. Atmospheric models of 210Pb are also of considerable interest to studies of global circulation and the long-range transport of atmospheric pollutants. The source of 210Pb is well-known and relatively constant on timescales of a year or more. It is thus an ideal tracer for studying atmospheric processes on these longer timescales (Baskaran 2011; Rehfeld & Heimann, 1995).

One of the key parameters controlling the distribution of 210Pb over the Earth’s surface is its residence time in the atmosphere. This has been estimated using a number of different methods. One of the earliest estimates (Burton & Stewart, 1960) used two different approaches. The first, based on mass balance arguments for the 210Pb inventory of a vertical column of air at Harwell in the UK, suggested a tropospheric residence time of around 17 days. The second, based on the activity ratios of 210Pb and its grand-daughter radionuclide 210Po, suggested values of 36 days from measurements in surface air at Harwell and 22-29 days from measurements on rainwater samples. Further measurements of the 210Po/210Pb activity ratio in surface air at Harwell carried out by Peirson et al. (1966) yielded a residence time of around 40 days. Since the measured values or ratios on which these calculations were based are unlikely to be representative of the atmosphere as a whole, and the equilibrium assumptions on which they were based unlikely to be realised, the validity of these results is highly uncertain.

Similar calculations were carried out by Poet et al. (1972) using the 210Bi/210Pb and 210Po/210Pb activity ratios in surface air and precipitation at Boulder, Colorado, and by Moore et al. (1973) using the 222Rn, 210Pb, 210Bi and 210Po activity ratios in tropospheric and lower stratospheric air at a range of continental sites over the United States. Residence times were calculated by assuming that the measured activities of 210Pb and its daughters arise from the decay of 222Rn in the atmosphere, and that their production and removal from the atmosphere are in steady state equilibrium. The parent/daughter relationship in the decay series was expressed by the equation

$$\dot{N}\_{2}=λ\_{1}N\_{1}-λ\_{2}N\_{2}-kN\_{2}=0$$

where *N1* and *N2* are the numbers of atoms of the parent and daughter, *1* and *2* their radioactive decay constants, and *k* a first order rate constant for the removal of aerosols from the atmosphere. 210Pb atoms are highly reactive and quickly attached to aerosol particles. It is reasonable therefore to suppose that the daughters are similarly attached and subject to the same removal rates.

Radionuclides are usually measured in terms of their activities (disintegrations per unit time), defined by *A1* = *1N1*, *A2* = *2N2*. In these terms the above equation becomes

$\dot{A}\_{2}=λ\_{2}\dot{N}\_{2}=λ\_{2}(λ\_{1}N\_{1}-λ\_{2}N\_{2}-kN\_{2})=λ\_{2}(A\_{1}-A\_{2})-kA\_{2}=0$ .

Applying this to 210Pb and its daughters, the relationships between them will be governed by the equations

 (1)

where *APb*, *ABi* and *APo* are the activities and *Pb*, *Bi*, *Po* their radioactive decay constants. Rearranging, the activity ratios will satisfy the equations (c.f. Moore et al. 1973):

,  (2)

Given the activity ratios, each of these equations can be solved to yield a value for the removal rate *k*. The 210Pb residence time will be *T* = 1/*k* (or ln*2*/*k* depending on the preferred convention). A similar approach was adopted by Gavini et al. (1974) who measured 210Pb, 210Bi and 210Po activity ratios in rain samples from Fayetteville, Arkansas, and by Carvalho (1995) who measured their concentrations in surface air at Lisbon, Portugal.

Table 1 summarises mean values of the 210Pb residence time calculated from the 210Bi/210Pb and 210Po/210Pb activity ratios in surface air and rainwater from the above studies. Possible causes of the large discrepancy between residence times calculated from 210Bi/210Pb ratios and those calculated from 210Po/210Pb ratios were thought to be inputs of older stratospheric air, or contamination by dust particles containing 210Pb, 210Bi and 210Po in secular equilibrium (Poet et al. 1972; Gavini et al. 1974). Assuming the main cause to be dust contamination, Poet et al. (1972) corrected their estimates of the mean atmospheric residence time to ~4 days for particles in the lower troposphere and ~7 days for particles in precipitation. Using various arguments, Gavini et al. (1974) suggested mean residence times of ~30 days for aerosols in the troposphere and ~1 year for the stratosphere. While some of the reasons advanced may be factors, the main cause of error is almost certainly failure of the 210Pb, 210Bi and 210Po activities in the samples to satisfy the equilibrium conditions implicit in equations (1). Since the concentrations of these radionuclides vary considerably with both geographical location and altitude, it is likely that their ratios will show similar variations. The main objective of this research is to model these variations and match the results to empirical data. This will provide a more accurate estimate of the 210Pb atmospheric residence time, while also producing a simple yet reliable model of the distribution of fallout 210Pb over the landscape.

**Table 1**

Atmospheric residence times calculated from 210Pb, 210Bi and 210Po activity ratios in surface air and rainwater.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Residence time from |  |  |
|  | 210Bi/210Pb | 210Po/210Pb | Location | Reference |
| Surface air | 5 d | 24 d | Boulder, Co | Poet et al. 1972 |
|  | 9 d | 24 d | Continental USA  | Moore et al. 1973 |
|  | 6 d |  33 d | Lisbon, Portugal | Carvalho 1995 |
|  |  |  36 d | Chilton, UK | Burton & Stewart 1960 |
|  |  |  40 d | Chilton, UK | Peirson et al. 1966 |
| Rainwater | 8 d | 19 d | Boulder, Co | Poet et al. 1972 |
|  | 17 d |  32 d | Fayetteville, Ark | Gavini et al. 1974 |
|  |  | 22-29 d | Chilton, UK | Burton & Stewart 1960 |

**2. Model equations and assumptions**

The radioactive gas 222Rn enters the atmosphere via exhalation from the land surface. Its subsequent distribution in the atmosphere is controlled by processes of advection, diffusion, and radioactive decay. The distributions of the 222Rn daughters 210Pb, 210Bi and 210Po are also influenced by the process of fallout. On short time-scales (hours or days), these processes can only be accurately described by using detailed 3-dimensional models (e.g. Feichter et al. 1991, Liu et al. 2001). Such models suffer from two major disadvantages, they are very computationally intensive, and over many parts of the world there is very little empirical data against which they can be validated. They are also highly dependent on the extent to which the processes and parameterizations on which they are based are accurate representations of real world processes. An international workshop (Rasch et al. 2000) comparing different global models found that they produced significantly different results for the atmospheric distribution of 210Pb.

On longer time-scales (time-averaged over a year or more), some of the essential features of the available empirical data have been captured using simpler models in which conservation principles are applied to a notional vertical column of air moving horizontally over the Earth’s surface, with little net transfer between adjacent columns (Jacobi & André 1963, Turekian et al. 1977). Piliposian and Appleby (2003) presented a more detailed model that took account of the vertical distribution of 222Rn and 210Pb in the atmosphere. Here we extend that work to include distributions of the 210Pb daughters 210Bi and 210Po, and the 210Bi/210Pb and 210Po/210Pb ratios used in studies of atmospheric residence times.

 *2.1 Mass balance equations and models*

In view of the potential complexity in solving these simplified equations, it will be useful to consider first the associated mass balance equations. Apart from providing some justification of the validity of the simplified model, they can also be used as a means for checking the validity of the numerical solutions.

If F denotes the mean global flux (per unit area) of 222Rn from the Earth’s land surfaces, the mean supply rate to the atmosphere as a whole will be *AL*F where *AL* is the effective area of the Earth’s land surface contributing to this flux. The global 222Rn inventory in the atmosphere with activity denoted by *QRn* will satisfy the balance equation

$\dot{Q}\_{Rn}=A\_{E}F-λ\_{Rn}Q\_{Rn}$ . (3)

The global inventory of the 222Rn daughter 210Pb, the activity of which is denoted by *QPb*, will similarly satisfy the balance equation

$\dot{Q}\_{Pb}=λ\_{Pb}Q\_{Rn}-λ\_{Pb}Q\_{Pb}-A\_{E}P$ (4)

(c.f. equations (1)) where *P* is the mean 210Pb fallout rate from the atmosphere and *AE* the area of the Earth’s surface over which it is distributed. These equations exclude any supported 210Pb, normally a small fraction, present on atmospheric dust particles. 210Pb dating is concerned only with the unsupported component.

It is reasonable to suppose that on timescales of a year or more the global inventories are in a state of near equilibrium, that is, $\dot{Q}\_{Rn}=\dot{Q}\_{Pb}=0$. Assuming further that the mean 210Pb fallout rate is proportional to the global 210Pb inventory we can write

 (5)

where *kg* is a mean global loss-rate coefficient. It then follows that the global 222Rn inventory can be written



and the mean 210Pb fallout rate

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Estimates of the 210Pb atmospheric residence time suggest that it is measured in days or at most weeks, and so is negligible compared to the radioactive 210Pb half-life (22.26 years). The radioactive decay constant *Pb* will accordingly be negligible compared to the loss rate *kg*. It follows that to a close approximation the above equation can be written

. (6)

If the 222Rn emanation rate and decay constant are measured in Bqm-2 d-1 and d-1 and the 210Pb decay constant measured in y-1, from dimensional arguments this equation will give the 210Pb flux in Bqm-2 y-1.

Although applicable to the atmosphere as a whole, since there is relatively little exchange between the Northern and Southern Hemispheres these equations are to a good approximation also applicable to the two hemispheres separately. Whereas inter-hemispheric exchanges take place on timescales of a few years (Junge 1962), the atmospheric residence times of these radionuclides are measured in days or weeks. Estimates of the mean 222Rn exhalation rate from land surfaces vary from ~0.7 atom cm-2 s-1 (Israël 1951) to ~1.2 atom cm-2 s-1 (Turekian et al. 1977). Although the rate will be highly variable on small spatio-temporal scales, it is reasonable to suppose that mean values on longer time-scales of a year or more will be relatively constant (c.f. Feichter et al. 1991, Liu et al. 2001). Here we assume a value of 1570 Bq m-2 d-1 (0.87 atom cm-2 s-1) determined from the atmospheric inventories at continental sites where the vertical distribution is close to the equilibrium state (Piliposian, & Appleby 2003). This approach does in principle integrate inputs from all sources over large geographical areas. Global balances have been calculated by applying the above figure to the c.74% of Earth’s continental land surface free of ice sheets, permafrost and fresh water bodies (~1.1×108 km2). We have also assumed an exhalation rate of ~10 Bq m-2 d-1 (Wilkening & Clements 1975) from the oceans (~3.62×108 km2). Given that ~70% of the ice-free land is in the Northern Hemisphere, the mean 210Pb flux from the atmosphere is calculated to be ~80 Bq m-2 y-1 in the Northern Hemisphere and ~38 Bq m-2 y-1 in the Southern Hemisphere. Considering the fact that information on 210Pb fallout over much of the Earth’s surface (and particularly the oceans) is very sparse, these figures are relatively consistent with values determined from the Liverpool University ERRC (Environmental Radioactivity Research Centre) global database on 210Pb fallout. The ERRC holds one of the world’s most comprehensive collection of 210Pb fallout data, accumulated over a period of more than 30 years as part of the program of 210Pb dating. These data suggest a mean 210Pb flux of ~73Bqm-2y-1 in the Northern Hemisphere and ~39Bqm-2 y-1 in the Southern Hemisphere (Appleby & Piliposian, 2010).

Data from sites in continental USA, Europe and Asia lying within the largely ice-free northern mid-latitudes (30o-65oN) suggest that the 222Rn-210Pb cycle (measured on long time-scales) is largely self-contained in this zone. Since dry land occupies around 51% of this total area it follows from equation (6) that 222Rn exhalation would if contained generate a mean 210Pb flux of 139 Bqm-2y-1. The mean empirical value from our database is ~136Bqm-2y-1. Given that intrahemispheric mixing is thought to take place on timescales of a few months (Warneck 2000), this approximate balance (though once again keeping in mind the sparsity of the data) is again consistent with the notion that 210Pb has a relatively short tropospheric residence time. The distribution of fallout within this zone is however strongly influenced by the major continental land masses. Driven by the predominantly west-to-east global circulation, air masses arriving at the western margins of North America and Eurasia are depleted in 222Rn and 210Pb during their passage over the Pacific and Atlantic oceans but replenished by 222Rn exhalation during their passage over the land masses. This is demonstrated by the regional data on mean annual fallout of 210Pb in North America and Eurasia shown in Figure 1. Fallout data from the Liverpool University ERRC database (encompassing data from around 250 sites) has been grouped together on a regional basis and mean values calculated for each region. 210Pb fallout has its highest values near the eastern margins of the continental land masses where the flux can exceed 200Bqm-2y-1 (per meter of rainfall).



**Figure 1.** Mean annual fallout of 210Pb (normalised against rain) at sites in North America and Eurasia extracted from the Liverpool University ERRC global database. Each point represents the average value for all fallout data within a given geographical region.

A similar distribution was obtained theoretically by Turekian et al. (1977) by applying mass balance principles to a notional vertical column of air moving over the Earth’s surface at northern mid latitudes. The model assumed a predominately west-to-east global circulation, a steady circulation velocity, a uniform 222Rn exhalation rate from land surfaces and negligible emissions from the oceans. It also assumed a mean 210Pb residence time of 5 days. Writing *QRn* and *QPb* for the radionuclide inventories of the column per unit area the calculations in effect solved equations (3)−(5) to determine variations in the 210Pb flux P with longitude.

*2.2 Transport processes within the air column*

A major limitation of mass balance models is that they give no information about the vertical distribution of the radionuclides within the column. Nor do they take into account the reservoir effect of the stratosphere. The fallout equation (5) is only applicable to that component of the 210Pb distribution lying within the troposphere. A significant stratospheric component built up during passage over major land masses is slowly released to the troposphere as the air column moves out over large water bodies and the troposphere becomes depleted by fallout. The principal mechanism controlling the vertical distribution of 222Rn and its daughters within an air column will be turbulent diffusion (Jacobi & André 1963). Since 222Rn (half-life 3.825 days) is an inert gas it is removed from the column only by radioactive decay. Assuming a Lagrangian coordinate system imbedded in the column, its distribution will thus satisfy the partial differential equation

  (7)

where *CRn*(*z,t*) denotes the 222Rn concentration (in Bq m-3) at altitude *z* and time *t*, *D* is an effective vertical diffusivity, and *λRn* is the 222Rn radioactive decay constant. The boundary conditions are

 (8)

where F denotes the 222Rn flux (in Bq m-2) by emanation from the Earth’s surface into the base of the column. In contrast to 222Rn, 210Pb atoms are highly reactive and readily adsorbed onto dust particles, and may be removed from the atmosphere by wet and dry deposition, as well as by radioactive decay to its daughter radionuclides 210Bi (half-life 5.013 d) and 210Po (half-life 138.4 d). Adding terms for this process, the 210Pb concentration *CPb*(*z*,*t*) (in Bq m-3) will be governed by the partial differential equation

  (9)

and boundary conditions

 (10)

where Λ(*CPb*) is a term characterizing the rate at which 210Pb condenses from the aerosol state dominated by turbulent diffusion to incipient precipitation dominated by gravity. In Piliposian and Appleby (2003) equations (7)−(10) were solved numerically, assuming a constant diffusivity D=2.7km2 d-1 (3.1×105cm2 s-1) and a mean 222Rn flux from land surfaces of 1570Bqm-2d-1. The values of these parameters were determined from vertical 222Rn distributions at sites where this radionuclide appeared to have reached equilibrium. The fact that the mean empirical profiles at these sites could be represented by an exponential relation suggests that the assumption of a constant diffusivity is a reasonable first approximation. We follow Piliposian and Appleby (2003) in supposing that droplet formation occurs only in the troposphere. The value of the term Λ(*CPb*) characterizing the rate at which 210Pb condenses from the aerosol state is thus effectively zero in the stratosphere. Its value in the troposphere was assumed to be proportional to the 210Pb concentration and so could be written

Λ(*CPb*) = ***CPb* {1–H(*z*–*z*1)}

where ** is a tropospheric removal rate constant, H(*z*) the Heaviside function defined by

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and *z*1 the height of the tropopause. The reciprocal of ** is a measure of the tropospheric residence time. It is again important to emphasise that these equations and concepts are only meaningful when applied to quantities time-averaged over sufficiently long time-scales to smooth out short-term fluctuations. For numerical calculations it was more practical, both from a mathematical and physical point of view, to replace the Heaviside function by the differentiable function

 $\frac{1}{2}\left(1+\tanh((βz))\right)$ ,

whence

 $Λ\left(C\_{Pb}\right)=κC\_{Pb}\left\{ \frac{1}{2}\left(1-\tanh((βz))\right)\right\}$.

This will give a transition zone at the tropopause of thickness ** across which the value of the term

 $\frac{1}{2}\left(1-\tanh((βz))\right)$

in the condensation function declines from 0.95 to 0.05 provided ** is chosen so that
** > 3/**.

The transport processes for 210Bi and 210Po can reasonably be presumed to follow those of 210Pb. Much of their production will take place after 210Pb atoms have become attached to dust or aerosol particles. The atmospheric concentrations of 210Bi and 210Po (in Bq m-3) can thus be assumed to satisfy the partial differential equations

 (11)

 (12)

together with the boundary conditions

, (13)

. (14)

Here we solve these equations numerically and use the results to calculate the distributions of the isotope ratios 210Bi/210Pb and 210Po/210Pb for different values of the tropospheric removal rate constant**. The results are compared with the available empirical data in order to determine the extent to which these data can be used to provide a good estimate of the tropospheric residence time.

**3. Numerical approach**

The value of the 222Rn flux F in the boundary condition (8) for equation (7) will depend mainly on whether the column is moving over land or water. Exhalation rates from oceans are estimated to be two orders of magnitude less than those from ice-free land surfaces. Although the distributions of 222Rn and its daughter radionuclides 210Pb, 210Bi and 210Po for the case of a prolonged 222Rn flux F into the base of the column can be obtained by using the MATHEMATICA software to solve *ab initio* the system of partial differential equations and boundary conditions (7)−(14), a numerically more stable solution is obtained by using a Green’s function approach, whereby we first consider the response of the system to a brief impulsive input of 222Rn

 (15)

where **(*t*) is the Dirac delta function. The response to a prolonged 222Rn input can then be constructed by representing it as a series of discrete inputs and superimposing the responses to different inputs at different times.

Under conditions of a constant diffusivity the 222Rn distribution for a brief impulsive input has the exact analytical solution

 (16)

where

 (17)

is the response to a unit input at time *t* = 0 (Piliposian &Appleby 2001). Substituting this function into equation (9) the three partial differential equations for 210Pb, 210Bi and 210Po were solved in turn numerically to give three Green’s functions

, ,  (18)

characterising the further responses of the system to an impulsive 222Rn input. Numerical calculations of these functions have been carried out for values of the tropospheric removal rate constant ** ranging from 0.08 d-1 (12.5 days residence time) to 0.3 d-1 (3.3 days residence time).

For a prolonged 222Rn flux F(*s*) (0<*s*<*t*), noting that the contribution of the amount of 222Rn injected into the atmosphere at time ** during the time interval d** to the 222Rn distribution at time *t* will be



 the 222Rn distribution has an exact analytical form

 . (19)

The distributions of the daughter radionuclides can similarly be written

 (20)

though these must be determined numerically. The procedure used for carrying out these calculations is given in the Appendix A. The validity of the solutions has been checked very carefully using mass balance arguments, by comparison with the equilibrium 222Rn distribution for a constant 222Rn flux over a long period of time, and also by comparison with standard numerical solutions of the governing equations using MATHEMATICA. Although the two methods were in good agreement over short to medium time-scales, the Green’s function method was numerically much more stable over long time-scales, where 222Rn concentrations had decayed to very low values.

**4. Global equilibrium distribution for northern mid-latitudes**

The above approach is used here to model the mean annual distribution of the 222Rn daughters 210Pb, 210Bi, and 210Po in the atmosphere at northern mid-latitudes. The results are fitted to the available empirical data in order to determine a best value for the removal rate constant **. From a model validation point of view these regions, defined as 30o–65o N spanning continental USA and Western Europe as far north as central Scandinavia (Fig. 2), have the advantage of a relatively good coverage of data on the distribution and fallout of 210Pb (Fig.1). They also cover virtually all the available empirical data on the daughter products 210Bi and 210Po (Table 1).



**Figure 2**. Map of the Earth’s northern hemisphere showing the land lying between 30o–65 o N. Also shown are the approximate transit times across the major land masses and oceans for a notional air column moving from west to east.

Although 222Rn exhalation rates from land surfaces are subject to short-term seasonal and weather-related fluctuations, mean annual inputs to the atmosphere will be relatively constant on longer timescales of a year or more. On these timescales the mean annual spatial distributions of the 222Rn daughters 210Pb, 210Bi, and 210Po will also be similar from year to year. The distribution within a notional column moving from west to east may thus be assumed to be a periodic function of longitude **(period 360o), or equivalently, of the time *t* with a period equal to the global transit time *T*. Using estimates from a range of different sources, Piliposian and Appleby (2003) estimated the mean annual global transit time to be around 78 days. Since the largely ice-free land within these northern mid-latitudes occupies roughly 51% of the total area, on each circuit and the column would spend 40 days over land and 38 days over the ocean. To a reasonable approximation, this can be divided into 11 days over North America, 16 days over the Atlantic, 29 days over Eurasia, and 22 days over the Pacific. Assuming a 222Rn exhalation rate over land of F=1570 Bqm-2 d-1, and negligible inputs from the oceans, the 222Rn exhalation rate into the base of the column will be

F(*t*) =F{H(*t*−*t*0) − H(*t*−*t*1)+ H(*t*−*t*2) − H(*t*−*t*3)} (21)

where *t*0 is the time at which the column crosses the western seaboard of North America, *t*1 the time at which it crosses the eastern seaboard, *t*2 the time at which it crosses the western seaboard of Europe, and *t*3 the time at which it crosses the eastern margin of the Eurasian land mass. For numerical calculations the Heaviside function H(*t*) can be approximated by the differentiable function

 $\frac{1}{2}\left(1+\tanh((αt))\right)$

where the value of the parameter ** is chosen so as to give suitably small transition zones across seaboards.

*4.1 Equilibrium Green’s functions*

Solving the governing partial differential equations (7)−(14) starting from a zero initial condition, in order to determine the equilibrium (periodic) distribution it would be necessary to track the solution over several circuits of the globe. This approach can however result in the build up of significant numerical errors. The process can be simplified, and made more accurate by introducing the notion of an equilibrium Green’s function.

Each time the column passes a fixed point on the Earth’s surface it will receive a brief impulsive input of 222Rn from that point the strength of which we denote by *I*0. Setting the time *t*=0 just as the column passes this point, the distribution of 222Rn in the column at times *t*>0 due to the input from this location at time *t*=0 will be *I*0*GRn*(*z,t*) (equation (16)). The distribution at time *t* due to the input from the same location on the previous circuit (at time −*T*) will be *I*0*GRn*(*z,t+T*). Adding the contributions from inputs on all previous occasions (at times −*kT*, *k* = 0,1,2,…), the distribution in the column at times 0<*t*< *T* due to present and past inputs from this location will be

 $I\_{0}\left\{G\_{Rn}\left(z,t\right)+G\_{Rn}\left(z,t+T\right)+G\_{Rn}\left(z,t+2T\right)+\cdots \cdots \right\}=I\_{0}G\_{Rn}^{equ}(z,t)$ (22)

where

 (23)

represents an equilibrium Green’s function for the 222Rn distribution. Since the distribution at time *t+T* will be the same as the distribution at time *t,* this function will be a periodic function of period *T*.

The solutions for the 222Rn daughters due to this impulse can be similarly written as periodic functions

 (24)

where *GPb*(*z,t*), *GBi*(*z,t*), *GPo*(*z,t*) are the corresponding Green’s functions for a single impulsive input. The equilibrium Green’s functions   are easily generated by continuing to add terms from previous circuits, up until the values are negligible. In practice we found that 6 periods were sufficient for the longer-lived 222Rn daughters, although because of its short half-life, one period (78 days) was sufficient for 222Rn itself.

Using this concept, the contribution to the equilibrium of 222Rn distribution at longitude ** due to 222Rn emissions from the Earth’s surface lying between longitudes ** and *−*** will be



where F(**) is the 222Rn exhalation rate at longitude **, *s* is the travel-time in a west-to-east direction to reach longitude ** , and *s* is the time taken for the column to traverse the incremental longitude **. If *V* (= 360o/*T*) is the circulation velocity, so that
**=***−**Vs* and *s*=**/*V*, the equilibrium 222Rn distribution at longitude ** will include all such contributions, and will thus be

  . (25)

The equilibrium distributions of the daughter radionuclides can similarly be written

 . (26)

The numerical procedure for carrying out these calculations is given in Appendix A.

**5. Results**

*5.1 210Bi/210Pb and 210Po/210Pb concentration ratios in ground-level air*

Figure 3 plots modelled values of the 210Bi/210Pb and 210Po/210Pb concentration ratios in ground-level air at mid-latitudes as functions of longitude ** for values of the tropospheric removal rate constant ** ranging from 0.08d-1 to 0.2d-1 calculated using equations (26). Also shown are mean empirical values calculated from all the measurements of 210Pb, 210Bi and 210Po in ground level air carried out at sites in Colorado (~105o W, Poet et al. 1972), Lisbon Portugal (~9o W, Carvalho 1995) and Hawaii (~156o W, Moore et al. 1974) and from 210Pb and 210Po measurements at Harwell UK (~1o W, Burton & Stewart 1960; Peirson et al. 1966).



**Figure 3.** Modelled values of the 210Bi/210Pb (left-hand axis) and 210Po/210Pb (right-hand axis) activity ratios in ground-level air at northern mid-latitudes plotted versus longitude for values of the tropospheric removal rate constant ranging from 0.08 d-1 to 0.2 d-1, showing also the major land masses. Mean activity ratios for Hawaii, the interior of the USA, and the western margin of Europe calculated from all the available empirical data are shown by the symbols ○ (210Bi/210Pb) and □ (210Po/210Pb). Unsupported activity ratios are represented by the solid symbols (•, ■).

It is evident from these results that for any given value of ** the theoretical 210Bi/210Pb and 210Po/210Pb concentration ratios vary considerably, the variations largely being governed by the position of the air column relative to major land masses. The 210Bi/210Pb ratio increases rapidly over large oceans to values close to unity (radioactive equilibrium). Renewed 210Pb production at the western margins of the major land masses causes its value to fall dramatically, reaching a minimum value after approximately 4 days in the case of **=0.2 (minimum value 0.23) or 7 days in the case of **=0.08 (minimum value 0.43). As the column moves further into the land mass, increased 210Bi production results in a gradual increase in the 210Bi/210Pb ratio. Reduced 210Pb production once the column has crossed the eastern seaboard and moves out over the ocean causes a sharp acceleration in the rate of increase. The 210Po/210Pb ratios follow a similar pattern though values are an order of magnitude lower due to the longer 210Po half-life.

Empirical values of the raw 210Bi/210Pb concentration ratio in surface air at the Colorado site ranged from 0.18-0.65 with a mean value of 0.41±0.02. Those at Lisbon ranged from 0.12-1.33 with a mean value of 0.57±0.10, whilst those at Hawaii at sea level on the windward side of the island ranged from 0.81-0.97 with a mean value of 0.84±0.03. The results from the Colorado and Hawaiian sites suggest that the value of ** lies between 0.08 and 0.1. Although measured results from Lisbon suggest a higher value of **, its position on the western edge of Europe where values of the 210Bi/210Pb concentration ratio change rapidly with distance makes the use of data from this location highly problematic. Further, the mean value may well be significantly influenced by local prevailing factors. 210Bi/210Pb values at this site determined during times of westerly air flows will have much higher values than those determined during times of easterly conditions.

210Po/210Pb ratios are an order of magnitude lower than the 210Bi/210Pb ratios. Raw values at ground-level at the Colorado site ranged from 0.03-0.25 with a mean value of 0.082±0.012. Those at Lisbon ranged from 0.03-0.78 with a mean value of 0.17±0.05. The mean value at Harwell, also a problematic location, was 0.16±0.05. At Hawaii the 210Po/210Pb ratio at sea level on the windward side of the island ranged from 0.08-0.18 with a mean value of 0.10±0.01. Although these results appear to suggest a significantly lower value of **, the most likely explanation for the discrepancy would appear to be contamination of samples by ground-level dust containing supported 210Pb and its daughters in radioactive equilibrium (Poet et al. 1972; Baskaran 2011). Writing *p*=226Ra/210Pb for the supported 210Pb fraction the unsupported activities will be (1−*p*)210Pb, 210Bi−*p*210Pb, 210Po−*p*210Pb. The amount of supported activity can then be estimated by adjusting the value of *p* so that the unsupported 210Bi/210Pb and 210Po/210Pb activity ratios yield the same value of **. The results of these calculations, shown in Table 2, suggest a relatively low amount of supported 210Pb, varying from 3.4% to 5.3% of the total 210Pb activity. Because of the low 210Po activities this correction has a disproportionate effect on the 210Po/210Pb ratio, as shown in Figure 3. The effect on the much higher 210Bi/210Pb ratio was relatively insignificant. Excluding the data from the West-European seaboard (Lisbon and Harwell) the value of ** was calculated to be between 0.09±0.02d-1 (Hawaiian data) and 0.11±0.01d-1 (Colorado data).

*5.2 210Bi/210Pb and 210Po/210Pb tropospheric inventory ratios*

 Figure 4 shows modelled values of the 210Bi/210Pb and 210Po/210Pb tropospheric inventory ratios calculated for values of the tropospheric removal rate constant ** ranging from 0.08d-1 to 0.2d-1. The results follow a similar pattern to those for ground-level air. 210Bi/210Pb ratios increase rapidly over large oceans to values close to radioactive equilibrium, but then fall steeply as the column arrives at the western margins of the major land masses. Minimum values over the land masses are reached after around 6 days in the case **=0.2d-1 (minimum value 0.32) or 10 days in the case **=0.08d-1 (minimum value 0.53).  210Po/210Pb ratios are again an order of magnitude lower than the 210Bi/210Pb ratios.



**Figure 4**. Modelled values of the 210Bi/210Pb (left-hand axis) and 210Po/210Pb (right-hand axis) tropospheric inventory ratios at northern mid-latitudes plotted versus longitude. Values of the tropospheric removal rate constant range from 0.08 d-1 to 0.3 d-1, also showing the major land masses. Mean activity ratios for the interior of the USA and the western margin of Europe, calculated from all the available empirical data, are shown by the symbols ○ (210Bi/210Pb) and □ (210Po/210Pb). Unsupported activity ratios are represented by the solid symbols (•, ■).

Since the isotopic composition of the troposphere as a whole is likely to be reflected in the isotopic composition of rainwater, empirical measurements of the 210Bi/210Pb and 210Po/210Pb tropospheric inventory ratios are most readily made using rainwater samples. Measurements of 210Pb, 210Bi and 210Po in rainwater were carried out at sites in Colorado (~105o W, Poet et al. 1972) and Arkansas (94o W, Gavini et al. 1974). Measurements of 210Pb and 210Po in rainwater were carried out at Harwell (Burton & Stewart 1960). A more direct estimate of tropospheric inventory ratios can be made using measured profiles of 210Pb, 210Bi and 210Po in the atmosphere. Concentrations of these radionuclides at altitudes ranging from ground-level up to 17 km were determined by Moore et al. (1973) at a number of sites in continental USA ranging from Utah (~112o W) to Kansas (~95o W). Many of the measurements were repeated on a number of separate occasions. Tropospheric inventories calculated by combining all the atmospheric profiles yielded a mean 210Bi/210Pb ratio of 0.52±0.05. Values calculated from rainwater measurements at the Colorado site ranged from 0.48−0.84 with a mean value of 0.61±0.01. Those from the Arkansas site ranged from 0.32−1.05 with a mean value of 0.74±0.10. Averaging all these results, a best estimate of the mean 210Bi/210Pb tropospheric inventory ratio for the interior of continental USA is 0.62±0.04. Similar calculations of the mean 210Po/210Pb tropospheric inventory ratio for the interior of continental USA yielded values of
0.14±0.03 from the atmospheric profiles, 0.061±0.005 from the Colorado rainwater measurements, and 0.13±0.02 from the Arkansas rainwater measurements, with a mean value of 0.11±0.02. The Harwell rainwater measurements had a mean 210Po/210Pb ratio of 0.10±0.02.

The raw tropospheric 210Bi/210Pb ratio from the continental USA suggests a value of ** comparable to that determined from the ground-level data. The raw 210Po/210Pb activity ratio again suggests a much lower value, presumably due to the disproportionate effect of a small amount of supported activity estimated in this case to be just 4.4% of the total 210Pb activity. The corrected unsupported activity ratios are shown in Figure 4. These results, also given in detail in Table 2, yielded a value of ** = 0.09±0.01d-1 similar to that determined from the ground-level data. Averaging the results from both data sets, a best estimate of the tropospheric removal rate constant is 0.097±0.012d-1, corresponding to a residence time of 10.3 ± 1.2 days. In practice we round these figures to ** = 0.10d-1 and the residence time to 10 days.

**Table 2**

Mean values of the empirical 210Pb, 210Bi and 210Po activity ratios, supported 210Pb, corrected (unsupported) activity ratios, and the tropospheric removal rate determined by fitting the empirical data to the modelled values.

|  |
| --- |
|  *(a) Ground-level concentration ratios* |
|  | Raw values | Supported210Pb | Corrected values | ** |
| Longitude | 210Bi/210Pb | 210Po/210Pb | 210Bi/210Pb | 210Po/210Pb | d-1 |
| -156 | 0.84±0.03 | 0.10±0.01 | 3.4% | 0.84±0.03 | 0.067 | 0.09±0.02 |
| -105 | 0.41±0.02 | 0.082±0.012 | 5.3% | 0.38±0.02 | 0.030 | 0.11±0.01 |
| 0 | 0.57±0.10 | 0.17±0.05 | 4.4% | 0.55±0.10 | 0.13 |  |
| 0 |  | 0.16±0.05 | 4.4% |  | 0.11 |  |
|  *(b) Tropospheric inventories ratios* |
|  | Raw values | Supported210Pb | Corrected values | ** |
| Longitude | 210Bi/210Pb | 210Po/210Pb | 210Bi/210Pb | 210Po/210Pb | d-1 |
| -101 | 0.62±0.04 | 0.11±0.02 | 4.4% | 0.61±0.04 | 0.069 | 0.09±0.01 |
| 0 |  | 0.10±0.02 | 4.4% |  | 0.061 |  |
|  |  |  |  | *Mean value* | 0.097±0.012 |

NB: The standard errors given in this Table are based on the 1 counting errors reported in the original publications (Table 1).

**6. Reservoir effect of the stratosphere**

Although the theoretical tropospheric residence time of 210Pb and its daughters appears to be around 10 days, the practical residence time is significantly greater due to the reservoir effect of the stratosphere. 222Rn and its daughters are transported from the troposphere to the stratosphere when concentrations are higher in the troposphere. This process is reversed once tropospheric concentrations fall below those in the stratosphere. Figure 5 plots the tropospheric, stratospheric and total 210Pb inventories (including fallout) versus time, resulting from an impulsive ground-level 222Rn input of 1570 Bq m-2 at time *t* = 0, for the case ** = 0.1. The inventories were calculated by numerical integration of the 210Pb profiles given by the Green’s function *I*o*GPb*(*z,t*) (equation (18)) with *I*o =1570 Bqm-2. The good agreement of the total 210Pb inventory with the theoretical values determined from the mass balance equation

 , (27)

also plotted in Figure 5, demonstrates the accuracy of the numerical calculations. According to equation (27) the total 210Pb inventory should reach a maximum value of 0.74Bqm-2 after approximately 40 days, though 90% of this value is achieved after just 24 days. Production by 222Rn is then effectively zero, and thereafter the 210Pb inventory declines slowly in accordance with the 210Pb radioactive decay law.

From the numerical calculations the 210Pb inventory in the troposphere reaches a maximum value of 0.32 Bq m-2 after just 6 days. Up to around 40 days it then declines rapidly at a rate corresponding to an apparent residence time of around 13 days due mainly to a combination of reduced creation by 222Rn decay and loss by fallout. After around 22 days the tropospheric inventory falls below that of the stratosphere causing a reverse flux from the stratosphere. This becomes significant after around 60 days, slowing down the rate of decline in the troposphere and increasing the residence time of the remaining tropospheric inventory to around 25 days.

The stratospheric inventory reaches a maximum value of around 0.12 Bq m-2 after 19 days, at which point it is almost equal to that in the troposphere. It then begins a long slow decline due to depletion of the 222Rn and the reverse flux to the troposphere. This decline has a residence time of 25 days, similar to that of the tropospheric inventory, transport rates from the stratosphere to the troposphere then matching fallout rates from the troposphere. Fallout from the atmosphere has declined by 50% from its maximum value after around 18 days, 90% after around 40 days, and 99% after around 90 days. Given a mean global circulation velocity of around 360kmd-1 (corresponding to the global circulation time of 78 days), these results show that fallout originating in 222Rn inputs from a particular source reaches a maximum value after the column has travelled a distance of ~2000 km. It then falls to around 50% of this value after ~6500 km.

Assuming no stratospheric reservoir effect and that the removal constant ** applies to the atmosphere as a whole, the atmospheric inventory would be given by the equation

. (28)

This result, also plotted in Figure 5, shows that the reservoir effect only becomes significant after around 35 days.



**Figure 5.** 210Pb inventories in the troposphere and stratosphere versus time following the brief impulsive injection of 1570 Bq m-2 of 222Rn into the base of an air column, calculated from the vertical distribution of the 210Pb activity assuming a tropospheric removal rate coefficient of 0.1 d-1. Also shown are the total 210Pb inventories (including both the atmospheric and fallout components). Values are calculated from both the numerical solutions and the theoretical mass balance equation, assuming no stratospheric reservoir effect to the atmospheric inventory

**7 Discussion**

The results presented in this paper show that while the 210Bi/210Pb and 210Po/210Pb activity ratios can potentially provide important information on the 210Pb atmospheric residence time, the sampling location plays an imporatant role that must be taken into account. The 210Bi/210Pb ratios are probably the more reliable, being less influenced by traces of supported activity. Discrepancies between the 210Bi/210Pb and 210Po/210Pb ratios can be used to make small corrections for the supported activity. Although the 210Bi/210Pb ratios have their highest values in air masses approaching western continental margins, the rapid decline in values (especially at ground-level) as the column moves into the land mass makes the use of such locations highly problematic for model validation. The most suitable locations would appear to be the interiors of large land masses.

The most extensive and reliable 210Pb, 210Bi, 210Po datasets are those obtained from sites in the interior of continental USA. They include measurements carried out on atmospheric samples from a range of different altitudes, and rainwater. Comparisons between the empirical data and model values suggest that the tropospheric removal rate constant has a value between 0.09-0.11 d-1. Much higher 210Bi/210Pb ratios from the oceanic site were also consistent with the model predictions. The corresponding mean tropospheric residence time of 10 days is significantly longer than the value of between 4−7 days suggested by Poet et al. (1972) and less than 7 days suggested by Moore et al. (1973). These values were however based on the assumption that 222Rn and its daughters were locally in a state of radioactive equilibrium, governed by equations (1). It is also significantly longer than the value suggested by Piliposian and Appleby (2003) though that was largely based on a review of earlier estimates.

The results presented here also highlight the role played by the stratosphere in extending the practical residence time of 210Pb in the atmosphere. The reservoir effect of the stratosphere, capturing 210Pb when tropospheric concentrations are high and releasing it when they are low, significantly enhances the long range transport of 210Pb from its source locations. Figure 6 plots the modelled 210Pb flux versus longitude at northern mid-latitudes assuming a tropospheric removal rate of 0.1d-1 and a 78 day global transit time. The relatively high fluxes at the western margins of Europe and the USA are largely due to long range transport across the Atlantic and Pacific oceans respectively. The model values for these western margins (~60 Bqm-2 y-1 for Europe and ~55 Bqm-2 y-1 for the USA) are comparable to the empirical values for southern England reported by Burton and Stewart (1960) and Peirson et al. (1966), and for coastal regions of western USA reported by Monaghan et al. (1989). Atmospheric fluxes at specific localities within a given region will however be strongly influenced by local factors such as the mean annual rainfall.



 **Figure 6.** 210Pb flux at northern mid-latitudes versus longitude assuming a tropospheric removal rate coefficient of 0.1 d-1 and global circulation transit time of 78 days.

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**Appendix A: Numerical Algorithms**

**Calculation of the radionuclide distributions for a prolonged 222Rn flux**

In the case of a prolonged 222Rn flux F(t) into the base of the column, assuming a constant diffusivity the distributions of 222Rn and its daughter radionuclides 210Pb, 210Bi, 210Po, are given in terms of their respective Green’s functions by equations (19) and (20). In this section we develop a simple algorithm for evaluating these integrals using the numerically determined Green’s functions. Discretising the problem and using a time step *h* (in days), to a good approximation the case of a continuous input can be solved by representing the 222Rn flux as a series of discrete inputs *Im* = *Fmh* at the beginning of each time interval (*m*–1)*h*<*t*<*mh* where F*m* is the mean flux during that time interval and ** a small correction factor to compensate for any errors in the inventory at time *t*=*mh* due to radioactive decay during the time step. From equation (16), the 222Rn distribution in the column at time *t*=*nh* (the end of the *nth* time interval) due to input at the beginning of the *mth* time interval (time *t*=(*m−*1*)h*) is then

. (A1)

Assuming a constant flux during each time step the correction factor will be

 (A2)

The correction is ~10% if *h*=1d and ~1% if *h*=0.1d. Summing the contributions from all inputs during time intervals 1 through *n* the 222Rn concentration in the column at time *t=**nh* is

. (A3)

In the same way, the 210Pb, 210Bi and 210Po distributions at time *t=**nh* are

, (A4)

, (A5)

, (A6)

where *GPb*(*z,s*), *GBi*(*z,s*), *GPo*(*z,s*) are the (numerically determined) 210Pb, 210Bi and 210Po Green’s functions.

*Implementation*

Calculations were carried using the MATHEMATICA software package. Assuming that the atmosphere has a vertical height of 30 km divided into 1 km steps, the four Green’s functions were stored as arrays

GRN(31,N), GPB(31,N), GBI(31,N), GPO(31,N),

where N is the total number of time steps in the calculation. The values of GRN were calculated exactly using the formula

 . (A7)

The values of GPB, GBI, GPO were evaluated from the numerically determined Green’s functions

 , , . (A8)

The 222Rn exhalation rates were stored as a vector array F(N), where F(*j*) is the input at the beginning of the *jth* time step. The concentration profiles were stored in arrays

CRN(31,N), CPB(31,N), CBI(31,N), CPO(31,N)

where CRN(*i,j*), CPB(*i,j*), CBI(*i,j*), CPO(*i,j*) are the radionuclide concentrations at altitude *z=i* at the end of the *jth* time step. The entries for these arrays were calculated using the formulae

 . (A9)

Using these equations, a numerical solution can be constructed for any given distribution of the 222Rn exhalation rate F(t), any given value of the removal rate constant **, and any desired number of time steps N.

**Global equilibrium distributions**

The steady state distribution in a column moving from west to east will include steady state contributions from each part of the Earth’s surface it passes over. In particular, dividing the global circulation time *T* into *N* time steps *h* = *T/N*, the input during the *m*th time step can be approximated by a source of strength *Im* = *Fmh* where *Fm* is the value of the exhalation rate at time *s*=(*m*−1)*h*, the beginning of the *m*th time step. Noting that the equilibrium Green’s function is periodic of period *T* the contribution of exhalation from this geographical location to the equilibrium 222Rn distribution in the column at time *t=nh*, the end of the *n*th time step, can be written



The equilibrium 222Rn distribution at time *t=nh* due to inputs from all *N* steps is thus

. (A10)

The distributions of the daughter radionuclides 210Pb, 210Bi and 210Po can similarly be written

 . (A11)

*Implementation*

The four equilibrium Green’s functions were stored as arrays over two cycles

EGRN(31,2*N*), EGPB(31,2*N*), EGBI(31,2*N*), EGPO(31,2*N*)

where *N* is the number of time steps in each cycle,

,

 and

, , .

The 222Rn exhalation rates were stored as a vector array F(*N*) where F(*j*) is the input at the beginning of the *j*th time interval. The equilibrium concentration profiles were stored in arrays

ECRN(31,*N*), ECPB(31, *N*), ECBI(31,*N*), ECPO(31,*N*)

where ECRN(*i,j*), ECPB(*i,j*), ECBI(*i,j*), ECPO(*i,j*) are the radionuclide concentrations at altitude *z=i* at time *j*, the end of the *j*th time interval. The entries for these arrays were calculated using the formulae

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Author Contributions

The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

**Graphical Abstract**

