Radon Emissions to the Atmosphere and their use as an Atmospheric Tracer

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Declaration

I, Lynette Robertson, declare that this thesis was composed by myself, and that the work described was carried out by myself, except where stated otherwise in the text. The work presented here has not been submitted in any previous application for a degree.

Lynette Robertson

9/6/05
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Abstract

The naturally occurring radioactive gases $^{222}$Rn and $^{220}$Rn are widely used as atmospheric tracers in a variety of applications pertinent to the study of air quality and climate change, but their use in this context is generally limited by the lack of information on spatial and temporal distribution in their emissions. This research has focused on the measurement of $^{222}$Rn and $^{220}$Rn emissions from soils, and investigations of the temporal and spatial variability of radon emissions on various scales, in order to enable more effective use of these isotopes in atmospheric studies. The temporal variability of $^{222}$Rn and $^{220}$Rn emissions has been investigated on the short (day to day) and seasonal time scales, and the spatial variability of $^{222}$Rn emissions has been investigated on the local, regional and global scales. Temporal studies were carried out on a bare soil site (medium textured sandy-loam) using manual and automatic flux chambers, and measurements to investigate the spatial variability on the local and regional scales were carried out in North Britain. Global-scale patterns in $^{222}$Rn emissions were investigated by examining the latitudinal and longitudinal distribution of large-scale indirect $^{222}$Rn flux measurements published in the literature.

Methods of predicting the spatial distribution of $^{222}$Rn emissions and improving on current $^{222}$Rn source terms used in models have been explored as part of this research, namely the use of gamma dose rate as a proxy; modelling emissions using digital soils and geology data; and modifying the spatially homogeneous 1 atom cm$^{-2}$ s$^{-1}$ $^{222}$Rn source term generally assumed in modelling studies to account for a trend of decreasing $^{222}$Rn emissions with increasing latitude in the Northern Hemisphere. Novel approaches to measuring $^{222}$Rn and $^{220}$Rn fluxes by the closed chamber method have also been developed and compared with some existing methods.

Soil moisture content was the most important factor controlling $^{222}$Rn and $^{220}$Rn emissions in the short term, and water table depth was important for $^{222}$Rn emissions, but not for $^{220}$Rn. Soil temperature and atmospheric pressure were not important factors, and freezing of the soil surface to ~5 cm depth had no effect on $^{222}$Rn or $^{220}$Rn emissions. A fresh snow cover of ~4 cm depth had no effect on $^{222}$Rn or $^{220}$Rn emissions, but a significant reduction in $^{222}$Rn flux was observed when the snow cover became icy, after melting and refreezing. $^{222}$Rn emissions were normally distributed (CVs = 24-39%) and $^{220}$Rn emissions were approximately log-normally distributed (CV = 89%). A diurnal trend of peak $^{222}$Rn emissions in the afternoon (~1600 h) and a minimum in the early morning (~0800 h), was noted for a small dataset of $^{222}$Rn fluxes. The most likely cause of this diurnal trend is the diurnal cycle in evapotranspiration, but the diurnal variation in atmospheric turbulence could also be a contributing factor. On the seasonal time scale, $^{222}$Rn emissions varied by one third between lowest and highest values, and the $^{220}$Rn flux varied by a factor of ~2. $^{222}$Rn flux was found to be near-normally distributed on the local scale (CV = 55%), and approximately log-normally distributed on the regional scale (CV = 204%). Mean $^{222}$Rn fluxes recorded at 15 sites in North Britain range from < 1 Bq m$^{-2}$ h$^{-1}$ to ~230 Bq m$^{-2}$ h$^{-1}$. The median flux was 9.7 Bq m$^{-1}$ h$^{-1}$. The $^{226}$Ra content of the soil, which ranged from <3 Bq kg$^{-1}$ to 55 Bq kg$^{-1}$, was the most important factor controlling $^{222}$Rn emissions on this scale (r = 0.91, p<0.001). Gamma dose rate was also found to correlate strongly with $^{222}$Rn flux (r = 0.87, p<0.01). The analysis of large-scale $^{222}$Rn flux estimates published in the literature showed $^{222}$Rn emissions to decrease with increasing latitude in the Northern Hemisphere, from ~1 atom cm$^{-2}$ s$^{-1}$ (76 Bq m$^{-2}$ h$^{-1}$) at 30°N to 0.2 atom cm$^{-2}$ s$^{-1}$ (15 Bq m$^{-2}$ h$^{-1}$) at 70°N. This trend is probably due to a combination of an increasing proportion of wetlands and organic soils at higher latitudes, and regional gradients in the $^{226}$Ra content of the soil. A $^{222}$Rn emissions map of North Britain reproduced the main spatial pattern in emissions, but overall it significantly under-predicted the magnitude of fluxes. Modifying the spatially homogeneous 1 atom cm$^{-2}$ s$^{-1}$ $^{222}$Rn source term generally assumed in modelling studies to account for a trend of decreasing $^{222}$Rn emissions with increasing latitude in the Northern Hemisphere was found to significantly improve the prediction of $^{222}$Rn concentrations by a global chemistry-transport model (STOCHEM-Ed) overall i.e. globally, with the greatest improvement for locations north of 50°N, where the mean prediction/observation ratio was reduced from 2.8 to 0.87.

For more effective use of $^{222}$Rn and $^{220}$Rn in atmospheric studies, more systematic surveys of radon emissions are essential, and radon flux methodologies need to be calibrated and standardised.
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<td>$C_x$</td>
<td>Concentration of a target gas for which radon is used as a tracer</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Diffusivity in free air</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Soil effective diffusivity</td>
</tr>
<tr>
<td>$d$</td>
<td>Lag distance</td>
</tr>
<tr>
<td>$h$</td>
<td>Height (chamber)</td>
</tr>
<tr>
<td>$K$</td>
<td>Eddy diffusivity</td>
</tr>
<tr>
<td>$J_{Rn}$</td>
<td>Radon flux ($^{222}\text{Rn}$ or $^{220}\text{Rn}$)</td>
</tr>
<tr>
<td>$J_{Rn-222}$</td>
<td>$^{222}\text{Rn}$ flux</td>
</tr>
<tr>
<td>$J_{Rn-220}$</td>
<td>$^{220}\text{Rn}$ flux</td>
</tr>
<tr>
<td>$J_x$</td>
<td>Flux of a target gas for which radon is used as a tracer</td>
</tr>
<tr>
<td>$m_{Rn-222}$</td>
<td>Gradient of the linear regression through $^{222}\text{Rn}$ activities</td>
</tr>
<tr>
<td>$m_{[Rn-222 + Rn-220]}$</td>
<td>Gradient of the linear regression through total ($^{222}\text{Rn} + ^{220}\text{Rn}$) activities, after $^{220}\text{Rn}$ has reached an equilibrium activity concentration</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface area</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>$z$</td>
<td>Depth</td>
</tr>
<tr>
<td>$z^*$</td>
<td>Diffusion length</td>
</tr>
<tr>
<td>$z^d$</td>
<td>Relaxation depth</td>
</tr>
</tbody>
</table>
$z^w$ Water table depth

**Greek alphabet**

- $\alpha$ Alpha particle
- $\beta$ Beta particle
- $\gamma$ Semivariance
- $\varepsilon_T$ Total soil porosity
- $\theta$ Volumetric water content
- $\lambda$ Radioactive decay constant
- $\xi$ Gamma dose rate
- $\phi$ Regionalised variable
Chapter 1

Introduction

1.1 Background

Over the last few decades there has been a great deal of scientific interest in the radioactive gases $^{222}\text{Rn}$ (radon) and $^{220}\text{Rn}$ (thoron), which occur naturally in the environment as part of the $^{238}\text{U}$ and $^{234}\text{Th}$ decay series (Figures 1.1 and 1.2). This interest has been partly because of the realisation that exposure to high concentrations of these gases and their radioactive decay products indoors is a very significant health hazard (UNSCEAR, 2000; Abrahams, 2002), but also because of their increased usage as atmospheric tracers in a wide variety of applications, such as estimating the magnitude of surface-atmosphere trace gas fluxes (e.g. Levin et al., 1999; Conen et al., 2002) and evaluating atmospheric transport models (e.g. Rasch et al., 2000; Chevillard et al., 2002). Interest in $^{222}\text{Rn}$ also stems from its widespread use as a tracer of a variety of geophysical processes; for example, it has been used in a range of hydrogeological applications (e.g. Hamada and Komae, 1998; Burnett and Dulaiova, 2003; Oliveira et al., 2003) and in identifying active geological faults (e.g. Dehandschutter et al., 2002; Ioannides et al., 2003), and has been used extensively as an aid in monitoring and attempting to predict earthquakes and volcanic activity (e.g. Hauksson and Goddard, 1981; King, 1998; Baubron et al., 2002; Reddy et al., 2004; Thomas et al., 1986; Connor et al., 1996; Tedesco et al., 1996). This thesis is concerned with $^{222}\text{Rn}$ and $^{220}\text{Rn}$

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1 Radon also occurs naturally as $^{219}\text{Rn}$, as part of the $^{235}\text{U}$ decay series, but because of the very short half-life of this isotope (4 s), and the relatively small abundance of $^{235}\text{U}$ in the Earth's crust (~0.7%), this isotope generally does not exist in the atmosphere in any significant quantity (Nazaroff, 1992; Ball et al., 1991).
Figure 1.1. Uranium-238 decay series, showing the decay mechanism and half-lives of each radionuclide. Alpha and beta decay are indicated by $\alpha$ and $\beta$, respectively, and those radionuclides that are significant gamma emitters are indicated with an asterisk (Sources: Firestone et al., 1998; Tyler, 1994). $^{222}\text{Rn}$ is the only member of the decay series which is a gas (all other nuclides are solids).
Figure 1.2. Thorium-232 decay series, showing the decay mechanism and half-lives of each radionuclide. Alpha and beta decay are indicated by α and β, respectively, and those radionuclides that are significant gamma emitters are indicated with an asterisk. (Sources: Firestone et al., 1998; Tyler, 1994). ²²⁰Rn is the only member of the decay series which is a gas (all other nuclides are solids).

emissions to the atmosphere and their use as atmospheric tracers. In particular, this research has focused on the measurement of ²²²Rn and ²²⁰Rn emissions from soils, and investigations of the temporal and spatial variability of radon emissions on various
scales, for the purpose of enabling more effective use of these isotopes and their decay products in atmospheric studies.

1.2 Radon and thoron as atmospheric tracers

$^{222}\text{Rn}$ and $^{220}\text{Rn}$ are widely used as atmospheric tracers in a variety of applications which are pertinent to the study of air quality and climate change. The various transport processes are illustrated schematically in Figure 1.3. Applications of $^{222}\text{Rn}$, which has a half-life of 3.82 days and is produced from the decay of $^{226}\text{Ra}$ (Fig 1.1), include estimating the magnitude of surface-atmosphere exchanges of climatically important gases such as $\text{CO}_2$, $\text{N}_2\text{O}$ and $\text{CH}_4$ (e.g. Levin et al., 1999; Conen et al., 2002), and evaluating atmospheric transport models (e.g. Rasch et al., 2000; Chevillard et al., 2002). $^{222}\text{Rn}$ has also been extensively used to study the origin of air masses (e.g. Polian

![Figure 1.3. Schematic illustration of the various atmospheric transport processes for which $^{222}\text{Rn}$ and $^{220}\text{Rn}$ and their radioactive decay products are used as tracers.](image-url)
et al., 1986; Balanski and Jacob, 1990; Carvalho, 1995) and the long-range transport of pollutants (e.g.; Wyputta, 1997; Sakashita et al., 2004). $^{220}\text{Rn}$, which has a half-life of 56 seconds and is produced from the decay of $^{224}\text{Ra}$ (Fig 1.2), has often been used to quantify the turbulent diffusivity of the near-surface boundary layer (e.g. Ikebe and Shimo, 1972; Doi and Kobayashi, 1994; Lehmann et al., 1999), and as a tracer of landmass contact on the local scale (e.g. Polian et al., 1986; Whittlestone et al., 1992). $^{222}\text{Rn}$ and $^{220}\text{Rn}$ decay products (Figs 1.1 and 1.2) have also been used to study tropospheric mixing processes (e.g. Fujinami and Esaka, 1987; Carvalho et al., 1995; Lugauer et al., 2000), and $^{210}\text{Pb}$ has been used to investigate stratosphere-troposphere exchange (Lambert et al., 1990). Radon decay products, which quickly become irreversibly attached to aerosols, have also been extensively used to determine the residence time of atmospheric aerosol (e.g. Moore et al., 1973; Dueñas et al., 2004).

$^{222}\text{Rn}$ and $^{220}\text{Rn}$ are particularly useful as atmospheric tracers because of their relatively simple source and sink distribution and convenient half-lives, which are on the same order or longer (3.82 d and 56 s, respectively) than a number of atmospheric transport processes (Fig 1.3). Because of the ubiquitous nature of $^{235}\text{U}$ and $^{232}\text{Th}$ in the Earth's crust, $^{222}\text{Rn}$ and $^{220}\text{Rn}$ are emitted from the land surface all over, and at a relatively constant rate (at least compared to other gases emitted from the land surface, such as biogenically-produced $\text{CO}_2$, $\text{N}_2\text{O}$ and $\text{CH}_4$, which often exhibit a large degree of temporal and spatial variability). Radon emissions from the oceans, where radium is present in solution at concentrations about 1000 times less than in soils and rocks, are at least two orders of magnitude smaller than from the land (Wilkening and Clements, 1975; Zahorowski et al., 2004a). This strong contrast between emissions from the land surface and the oceans enables continental and oceanic air masses to be distinguished on the basis of their relatively high and low radon concentrations, respectively (e.g. Brunke et al., 2004). As radon is inert and relatively unsusceptible to wet deposition, its radioactive decay to polonium, which can easily be quantified from the known half-
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lives, is its only sink. However, the full potential of $^{222}$Rn and $^{220}$Rn and their radioactive decay products as tools for studying and quantifying atmospheric transport is currently not exploited, because of insufficient knowledge of the spatial and temporal distribution in radon emissions, particularly the spatial distribution of $^{222}$Rn at the regional and global scales. Although radon emissions from the land surface are generally fairly uniform compared to those of other surface-emitted gases, such as biogenically-produced N$_2$O, CO$_2$ and CH$_4$, in regions of complex geology, where there are large variations in the radium content of the soil, radon emissions may vary by more than two orders of magnitude (e.g. Nielsen et al., 1996; Whittlestone et al., 1996, 1998). Variations in the moisture content of the soil and water table depth can also cause a significant temporal variation in emissions (e.g. Conen and Robertson, 2002/Appendix A). Seasonal variations of a factor of two for $^{222}$Rn, and a factor of three for $^{220}$Rn have been reported (Schübler, 1996; Whittlestone et al., 1996, 1998). Thus, in order to obtain reasonably accurate radon 'source terms' for use in atmospheric studies, information on the spatial and temporal distribution in emissions is essential.

Although there has been a substantial amount of research into the subject of radon over the last 50 years, and there are many $^{222}$Rn flux measurements reported in the literature (reviews are provided in: Wilkening et al., 1975; Turekian et al., 1977; UNSCEAR, 1982; and Conen and Robertson, 2002), only a few systematic surveys of the spatial variability in $^{222}$Rn and $^{220}$Rn emissions have been carried out (Schery et al., 1989; Graustein and Turekian, 1990; Nielsen et al., 1996; Whittlestone et al., 1996, 1998; Jennings, 2003 - cited in WMO, 2004). Most flux measurements have been carried out as part of studies with a focus other than characterising the spatial distribution of radon emissions, with measurements limited to a few locations only. Health-hazard studies have focused on the measurement of radon concentrations in soil gas and indoors. $^{220}$Rn flux data are sparse in general, partly due to the greater analytical challenge of measuring this much shorter-lived isotope, but also because the importance of $^{220}$Rn as a
contributor to the natural radiation dose has not been acknowledged until more recently (UNSCEAR, 2000). Radon flux measurements have been carried out at different intensities, at different times, and with a wide range of equipment and methods. International intercomparison exercises of radon flux methodologies have shown coefficients of variation of 34% (Hutter and Knutson, 1998) and 43% (Neznal and Neznal, 2002a). Thus, it is difficult to precisely compare the radon fluxes reported in the literature.

Over the last decade or so the use of $^{222}\text{Rn}$ in atmospheric applications has grown significantly (Zahorowski et al., 2004b). The global network of $^{222}\text{Rn}$ observations has expanded (Barrie and Sommeria-Klein, 2004; Sanderson and Lee, 2004), and atmospheric model resolutions have improved substantially, thereby enabling more detailed modelling studies to be carried out. However, there has been little effort to improve on our knowledge of the spatial and temporal distributions of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ emissions. Given the observed spatial and temporal variability in radon emissions, and that the quality of atmospheric studies using $^{222}\text{Rn}$ and $^{220}\text{Rn}$ as tracers is largely dependent on the accuracy of the emission rates or ‘source-terms’ used in these studies (e.g. errors in trace gas flux estimates or modelled radon concentrations are largely proportional to the error in the radon source-term used), it is important that the spatial and temporal variability in emissions is taken into account in source terms. Currently, the most prominent applications of $^{222}\text{Rn}$ are the evaluation of atmospheric transport models (e.g. Rasch et al., 2000; Chevillard et al., 2002) and the estimation of regional-scale ($10^2$ to $10^5$ km$^2$) fluxes of climatically sensitive gases such as CO$_2$, N$_2$O and CH$_4$ (e.g. Dörr and Münnich, 1990; Levin et al., 1999; Biraud et al., 2000). $^{222}\text{Rn}$ is also increasingly being used to estimate trace gas fluxes on the local scale (0.1 to 10 ha) (e.g. Conen et al., 2002; Butterweck et al., 1994; Martens et al., 2004). $^{222}\text{Rn}$-tracer methods of measuring trace gas fluxes have the potential to substantially improve the long-term monitoring trace gas fluxes on the local and regional scales, as they provide much
cheaper alternatives to other techniques available, and can be used to obtain flux estimates under conditions when most micrometeorological methods are not valid, such as during nocturnal inversions and under forest canopies. However, as the error in the estimate of the target gas is directly proportional to the error in the $^{222}$Rn source term used, the accuracy of $^{222}$Rn-based flux estimates are directly dependent on the accuracy of the $^{222}$Rn source term used. Accurate estimates of the magnitude of trace gas fluxes are needed for national emissions inventories (which are now legally required in countries which have signed the Kyoto Treaty), and in climate and air pollution modelling studies, which are carried out using atmospheric transport models which have often been validated and parameterised using $^{222}$Rn. For example, regional-scale trace gas fluxes are increasingly being derived by inverse modelling (e.g. Gurney et al., 2002; Gimson and Uliasz, 2003).

1.3 Thesis objectives and structure

The overall aim of this research was to improve on the current state of knowledge on the temporal and spatial distribution of $^{222}$Rn and $^{220}$Rn emissions, so that these isotopes and their decay products can be used more effectively in atmospheric studies. This research has focused on the measurement of $^{222}$Rn and $^{220}$Rn emissions from soils and investigations of the temporal and spatial variability of these emissions on various time-scales. Methods of predicting the spatial distribution of $^{222}$Rn emissions and improving on current $^{222}$Rn source terms used in models have been explored, and novel approaches to measuring $^{222}$Rn and $^{220}$Rn fluxes by the closed chamber method have been developed and compared with some existing methods.

Throughout this work, $^{222}$Rn and $^{220}$Rn fluxes have been measured by the closed (or static) chamber method, using an AlphaGUARD PQ2000PRO radon monitor (ionisation chamber) for radon detection. Other research groups have used the AlphaGUARD in combination with closed chambers to measure $^{222}$Rn fluxes (e.g. Koarashi et al., 2000;
Ferry et al., 2001), and Lehmann et al. (2004) have measured $^{222}$Rn and $^{220}$Rn fluxes simultaneously using two AlphaGUARD instruments joined in series. The approach applied in this research is novel in that only one AlphaGUARD has been used to measure both the $^{222}$Rn and $^{220}$Rn flux simultaneously, thus providing a more economical alternative to the method of Lehmann et al. (2004). An automated system for the analysis of $^{222}$Rn in air samples has also been developed, to enable replicate measurements and studies of the spatial variation in $^{222}$Rn emissions in which measurements are independent of time. As far as is known, this is the first time this has been done. These methods are described in Chapter 3, after a review of literature relevant to this research in Chapter 2.

In Chapter 4, the results of studies carried out to investigate temporal variability of $^{222}$Rn and $^{220}$Rn emissions are reported and discussed. Temporal variations in $^{222}$Rn and $^{220}$Rn emissions have been studied on the short (<1 day to 1 week) and seasonal time scales, and the effects of variations in water table depth, freezing of the soil, and snow cover have been examined. Water table depth, a factor which is known to be important for other gases emitted or taken-up by the soil, does not appear to have been included in studies of radon emissions previously, and there are few and seemingly conflicting data on the effects of freezing of the soil and snow cover.

The spatial variability of $^{222}$Rn emissions has been investigated on the local, regional and global scales (Chapter 5). Local-scale studies have employed geostatistical methods of analysis, which do not appear to have been used in any studies of radon flux, but have been applied in a few investigations of the spatial variability of $^{222}$Rn in soil gas (Badr et al., 1989; Oliver and Badr, 1995; Oliver and Khayrat, 2001). Geostatistics provide powerful tools for investigating the spatial variability of environmental properties which vary continuously in space, and methods of spatial prediction (Webster and Oliver, 2001). These methods have been widely used in the fields of mineral exploration and
petroleum engineering for several decades, but it is only relatively recently that environmental scientists have begun to apply them to their research problems. The investigation of the spatial variability of $^{222}$Rn emissions on the regional scale has focused on North Britain, and has included measurements of the 'in-situ' terrestrial gamma dose rate. Gamma dose rate has been found to correlate reasonably well with $^{222}$Rn flux (Schery et al., 1989; Nielson et al., 1996), and indoor radon concentrations (Duval and Ottonm 1990; Poncella et al., 2004), but does not appear to have been used to predict $^{222}$Rn emissions. Given that gamma radiation is routinely monitored across large parts of the world as part of national radiation surveillance networks which have been set-up to detect dangerous levels of radiation in the event of a nuclear accidents, this correlation could prove a useful means of predicting the spatial distribution of $^{222}$Rn emissions on the regional-scale, especially for regions where the monitoring network is quite dense. Global-scale patterns in $^{222}$Rn emissions have been investigated by examining the latitudinal and longitudinal distribution of large-scale indirect $^{222}$Rn flux measurements published in the literature (Conen and Robertson, 2002/Appendix A).

In Chapter 6, a $^{222}$Rn emissions map of North Britain, which has been produced using the Food and Agriculture Organisation (FAO) digital soils map of the world and British Geological Survey (BGS) solid geology data is presented and discussed. Only a small number of studies have attempted to model the spatial distribution in $^{222}$Rn emissions on the regional-scale. Eckhardt (1990 - cited in Chevillard et al., 2002) produced a $^{222}$Rn emissions map of Europe using the FAO soils map of the world and spot measurements of $^{222}$Rn flux from around Europe, and Nielson et al. (1995 - cited in Chevillard et al., 2002) produced a flux map for the state of Florida, USA, using a similar approach. The only attempt at a global $^{222}$Rn emissions map is that produced by Schery and Wasiolek (1998), who modelled $^{222}$Rn emissions on a 1° by 1° grid. Because of the limited amount of $^{222}$Rn flux data and information on the relevant soil parameters required for modelling $^{222}$Rn emissions, these models are generally very crude and can only be considered as a
first (but nevertheless very useful) step towards providing a reasonably accurate spatial description of $^{222}$Rn emissions, and should therefore be interpreted with caution.

Chapter 7 is in the form of a scientific research paper which has been published in Tellus B (Robertson et al., 2005/Appendix B), entitled "Test of a northwards-decreasing $^{222}$Rn source term by comparison of modelled and observed atmospheric $^{222}$Rn concentrations". This study follows on from the investigation of the spatial variability of $^{222}$Rn emissions at the global scale (Chapter 5; Conen and Robertson, 2002/Appendix A). The purpose of this study was to find if using a $^{222}$Rn source term which incorporates a trend of decreasing $^{222}$Rn emissions with increasing latitude in the Northern Hemisphere, as indicated by large-scale indirect $^{222}$Rn flux estimates (Chapter 5; Conen and Robertson, 2002/Appendix A), improved predictions of $^{222}$Rn concentrations made by a global chemistry-transport model. Current practice is to assume a spatially homogeneous and constant $^{222}$Rn emission rate of 1 atom cm$^{-2}$ s$^{-1}$ from all ice-free land surfaces, and zero emissions from the oceans; however, it is generally acknowledged that this undifferentiated source term is limiting validations of atmospheric transport models. The model used in this study was STOCHEM-Ed, a new version of the UK Met Office global chemistry-transport model (Stevenson et al., 2003).

Finally, in Chapter 8 the most important findings of this research and their implications for atmospheric studies are discussed, and recommendations for further work are given.
Chapter 2

Literature review

2.1 Introduction

In this Chapter a review of the literature relevant to the present work is given. First, the state of knowledge on the processes of radon emanation and transport in soil, and the factors which control temporal and spatial variations in radon emissions from soils, are reviewed in sections 2.2 and 2.3, respectively. As this research is primarily concerned with the measurement of radon emissions from soils, and as soils are by far the largest source of the radon in the atmosphere (Turekian and Graustein, 2004), this review focuses on radon emissions from soils only. The oceans, rocks, and other geological sources such as volcanoes an geothermal systems, can be important sources locally, however (e.g. Zahorowski et al. 2004a; Sato, 2003; Dehandschutter et al., 2002), and industrial activities – the phosphoric acid and elementary phosphate industries in particular – can cause localised ‘hot-spots’ in radon concentrations (UNSCEAR, 2002). Radon emissions from the oceans, where radium is present in solution at concentrations about 1000 times less than in soils and rocks, are at least two orders of magnitude smaller than emissions from the land (Wilkening and Clements, 1975; Zahorowski et al., 2004a). A review of the behaviour of radon in the geological environment can be found in Ball et al., (1991). In §2.4 the various methods used for detecting radon and measuring its emission rate from soils are described, and in §2.5 studies which have been concerned with the temporal and spatial variability of $^{222}$Rn and $^{220}$Rn emissions are reviewed. Finally, in §2.6 the different atmospheric applications of $^{222}$Rn and $^{220}$Rn are reviewed.
2.2 Radon emanation and transport in soil

The transfer of radon from the soil to the atmosphere can be thought of as a two-part process involving first the escape or 'emanation' of radon from the radium-bearing mineral of the soil grain, and, secondly, its transport through the soil matrix and across the soil-atmosphere interface. These two processes and the factors which affect them are described in turn below.

2.2.1 Emanation

Emanation is the process by which radon is released from the radium-containing minerals of soil grains into the soil pore volume. When radon is produced (from the alpha-decay of radium - Figs. 1.1 and 1.2) there are three possible fates for the recoiling radon atom: 1) it remains imbedded in the mineral grain; 2) it travels across a pore space and becomes imbedded in another mineral; or 3) it enters the pore space fluids (Figure 2.1). As the recoil range of radon in minerals is very small compared to the average

Figure 2.1. Schematic illustration of radon recoil trajectories in and between soil grains. Radium atoms are indicated by solid circles and radon atoms by open circles. The dashed line indicates the recoil range, R, of radon atoms (0.02-0.07 μm for common minerals). At point A the radium atom is too deeply embedded within the grain for the radon atom to escape. At points B and D the recoiling radon atom possesses sufficient energy after escaping the host grain to penetrate an adjacent grain. At point C the radon atom terminates in the pore water (after Tanner [1980] and Nazaroff [1992]).
grain size, much of the radon produced remains imbedded in the soil grain, or, depending on the amount of water present in the soil pore space, it becomes imbedded in adjacent soil grains. Escape by diffusion from intact grains is negligible, as the diffusion distance is insignificant compared to the recoil distance (Tanner, 1964). Thus, only a fraction of the radon that is produced enters the pore volume of the soil, and thus has the potential to escape to the atmosphere. This amount is commonly referred to in the literature as the ‘emanating fraction’ of the soil.

As the recoil range of $^{222}$Rn in water is much less than that in air (0.1 μm for water and 0.63 μm for air), the emanating fraction increases with increasing soil moisture content (Strong and Levins, 1982; Stranden et al., 1984; Damjær and Korsbech, 1985). This effect is illustrated in Figure 2.2 for a sample of uranium ore tailings (Strong and Levins, 1982). At the lower soil moisture ranges, the relative increase in the emanation coefficient increases sharply with increasing moisture content, but, as the water saturation limit is approached, additional moisture in the pore volume has a diminishing

![Figure 2.2. Effect of soil moisture content on the relative $^{222}$Rn emanation coefficient for a sample of uranium ore tailings (Strong and Levins [1982], after Nazaroff [1992]).](image-url)
effect. Given that radon is relatively insoluble in water (aqueous-gaseous partition coefficients for $^{222}\text{Rn}$ between distilled water and air are: 0.506 at 0°C, 0.340 at 10°C, 0.245 at 20°C, and 0.193 at 31.6°C [Nazaroff, 1992]), radon present in the partially saturated pore volume may be transferred rapidly to the pore air volume. Thus, over the lowest soil moisture ranges an increase in soil moisture will tend to increase $^{222}\text{Rn}$ emissions, but at higher moisture levels the relative increase in the emanation coefficient is small, and therefore unlikely to lead to a significant increase in flux. Further, at higher soil moisture levels, the potential increase in $^{222}\text{Rn}$ emissions due to enhanced emanation is likely to be offset because of the reduced diffusivity of the soil. This is discussed in more detail below (§2.2.2). Adsorption coefficients for radon are generally low for moist soils (e.g. 0.05 at 10°C and 10% moisture [Schery and Whittlestone, 1989]), and theoretical estimates and laboratory studies show that adsorption of radon on soil grains decreases rapidly with increasing water content, becoming insignificant for water contents greater than about 30-40% (Rogers and Nielsen, 1999b).

The emanating fraction, or emanation coefficient, has been calculated for a wide range of soils, as well as various rocks and building materials (e.g. Megumi and Mamuro, 1974; Schery et al., 1982; Stranden et al., 1984; Damkjær and Korsbech, 1985). For soils it varies over a wide range: from < 5% to 70%, but is typically ~ 20% (Nazaroff, 1992). Emanation coefficients for rocks and building materials are generally much smaller in comparison because of their comparatively smaller pore spaces. Nazaroff et al. (1988) reported an average emanation coefficient in rock of 8.4% (cited in Washington and Rose, 1992). Besides moisture content, the most important factors determining the emanating fraction in soils are the distribution of radium in the soil grains (Tanner, 1980; Semkow and Parekh, 1990) and the specific surface area of soil grains, and thus the soil particle size distribution (Bossus, 1984; Semkow and Parekh, 1990). If radium is distributed uniformly in the mineral grains, the emanating fraction increases linearly with increasing specific surface area of the soil grain (Bossus, 1984),
and thus decreasing particle size. However, the relationship between grain size and emanating fraction is usually more complicated than this because of weathering processes (in particular the sorption or co-precipitation of radionuclides with metal oxides or organic compounds in grain coatings), which can cause radium to become concentrated in thin coatings on the surface of minerals (Tanner, 1980; Semkow and Parekh, 1990; Greeman and Rose, 1996; Schumann and Gunderson, 1996). Further, smaller soil grains tend to be enriched in radionuclides compared to larger grains, because of adsorption at the surface by clay minerals (Megumi and Mamuro, 1974, 1977). A number of other, more minor, factors have also been shown to affect the amount of radon escaping to the soil pore space, for example, damage to the crystal structure of the mineral caused by alpha-decay, and microscopic fractures and fissures within the mineral provide additional pathways for radon release (Morawska and Phillips, 1993; Semkow and Parekh, 1990). The emanating fraction has also been shown to be dependent on temperature (Stranden et al., 1984), however, over the range of temperatures common for soils this effect is unlikely to be an important factor for radon emanation (Nazaroff, 1992).

2.2.2 Transport
Like all other gases produced in the soil, radon migrates through the unsaturated soil zone mainly by molecular diffusion, except for in very porous or fractured soils, where advective transport (or mass flow) can also be an important process (Schery et al., 1984; Schery and Siegel, 1986; Dueñas et al., 1997). In the earlier years of research it was suggested by some investigators that thermal gradients in the soil were also an important factor i.e. convection was an important process for radon transport (Malakhov et al., 1966; Styra et al., 1970; Guedalia et al., 1970); however, except for in very porous or fractured soils, a significant transport effect due to the moderate thermal gradients experienced in soils is unlikely (Schery and Petschek, 1983). Transport of radon in the soil water phase is negligible, as the molecular diffusion coefficient is $\sim 10^4$ times
smaller in water than in air (Dueñas et al., 1997). Hence, for moist soils, diffusion through the air-filled pore spaces is by far the dominant mechanism of transport for radon, and the soil-atmosphere flux of radon, $J_{Rn}$, can therefore be described using Fick's first law:

$$J_{Rn} = -D_e \frac{\Delta A_{Rn}}{z}$$  \hspace{1cm} (2.1)

where $D_e$ is the 'effective' (or interstitial) diffusivity of radon in the soil and $\Delta A_{Rn}$ is the difference between the activity of radon in the atmosphere and the activity in the soil gas at depth $z$.

Because of deviations in pore direction from the overall direction of gas movement (tortuosity), the roughness of the pore surfaces, and the fact that interconnections between pore spaces may be blocked by water, $D_e$ is considerably smaller than the diffusivity of radon in free air, $D_0$ ($1.2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ for $^{222}\text{Rn}$). Values of $D_e$ for radon in porous media (soils, rocks, and building materials) vary over a wide range of several orders of magnitude, depending on the porosity of the material and its degree of water saturation. Typically, the value of $D_e$ for radon in soils with a low moisture content is $\sim 3 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, but in a fully-saturated soil $D_e$ may be as low as $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Nazaroff, 1992). Figure 2.3 shows values of $D_e$ calculated for radon, for three soils of different porosity (Rogers and Nielson [1999a], after UNSCEAR [2000]). With increasing soil water saturation $D_e$ diminishes, and above soil moisture contents of $\sim 50\%$ there is a proportionately greater reduction in diffusivity with increasing soil moisture content. In general, this effect causes radon emissions to decrease with increasing soil moisture content, except for very dry soils, where an increase in soil moisture content may cause an increase in radon emissions, because of enhanced emanation (§2.2.1).
$D_e$ has been related to $D_0$ and physical properties of the soil empirically and by modelling (Ball and Smith, 2001). For example, Rogers and Nielson (1991) related $D_e$ to total porosity:

$$D_e = D_0 \varepsilon_T \exp(-6\theta \varepsilon_T - 6\theta^{14\varepsilon_T})$$  \hspace{1cm} (2.2)

where $\varepsilon_T$ is the total porosity and $\theta$ is the volumetric water content; and, after Healy (1996), Conen and Smith (2000) proposed the relationship:

$$D_e = D_0 \theta^4$$  \hspace{1cm} (2.3)
Assuming a homogeneous soil with uniform porosity, the diffusion length - the mean distance over which an atom or molecule may travel in the soil during its lifetime - of a radioactive gas is given by:

\[ z^* = \sqrt{\frac{D}{\lambda}} \]  

(2.4)

where \( z^* \) is the diffusion length (m), and \( \lambda \) is the appropriate radioactive decay constant (s\(^{-1}\)) (Lehmann et al., 2000). Typical diffusion lengths for \(^{222}\)Rn and \(^{220}\)Rn in soils of medium texture and permeability are \( \approx \) 1 m for \(^{222}\)Rn and 1 cm for \(^{220}\)Rn (Nazaroff, 1992), but in deep and well-aerated soils the migration distance of \(^{222}\)Rn can be more than 2 m (Dörr and Münstich, 1990). \(^{222}\)Rn activity profiles for three soils of different depth and properties are shown in Figure 2.4. Activities increase asymptotically to a

![Graph of activity profiles](image)

**Figure 2.4.** Measured and modelled \(^{222}\)Rn activities for three soils of different depth and properties. Profiles (a) and (b) are from a sandy forested soil, and (c) is from an almost water-saturated clayey soil. As radon is inert and diffusion is the dominant transport mechanism, radon activities increase asymptotically to a constant value with increasing depth below the surface (Dörr and Münstich, 1990).
constant value with increasing depth below the surface. The depth at which the radon activity reaches an equilibrium value (where diffusional loss of radon can be neglected and radon production is equal to decay) is the 'relaxation depth' (Dörr and Münich, 1990). As radon is inert, the relaxation depth, \( z^d \), is equal to \( z^* \).

### 2.3 Factors causing temporal and spatial variations in radon emissions from soils

#### 2.3.1 Temporal factors

**Soil moisture content**

Variations in soil moisture content due to wetting and drying of the soil after rainfall are the most important cause of temporal variations in radon emissions on the short time scale (Ussler et al., 1994; Ferry et al., 2001), and are much more important for \(^{220}\)Rn because of its much shorter half-life and therefore diffusion length (§2.2.2). Although radon emanation increases with increasing soil moisture content (§2.2.1), except at very low soil moistures, an increase in soil moisture will generally lead to a reduction in radon emissions because of the reduction in the diffusivity in soil (§2.2.2). This effect is illustrated in Figure 2.5, showing the mean \(^{222}\)Rn flux over a range of soil moistures (Schery et al., 1989). Heavy rainfall can cause a marked or total reduction in emissions (Ussler et al., 1994; Ishimori et al., 1998; Ferry et al., 2001), after which there may follow a brief period where emissions are of much larger magnitude than average, as a result of an accumulation of radon in the soil (Ussler et al., 1994; Asher-Bolinder et al., 1990; Schery et al., 1984). The type of vegetation and degree of water saturation of the soil are important factors determining the impact of rainfall on radon emissions (Ussler et al., 1994; Chapter 4).
Figure 2.5. Radon flux versus moisture content of the soil at 20 cm depth. Due to the opposing effects of soil moisture on emanation and diffusion of radon, the radon flux initially increases and then decreases with increasing soil moisture content (Schery et al., 1989).

Water table depth
For soils with a relatively shallow water table (i.e. > 1 m depth), changes in water table depth are an important factor influencing $^{222}\text{Rn}$ emissions on the seasonal time-scale (Chapter 4/Conen and Robertson, 2002/Appendix A; Levin et al., 2002). More specifically, water table depth - $z^w$, will be an important factor for soils where $z^w$ is generally less than $z^d$, the relaxation depth of radon (§2.2.2). Conen and Robertson (2002) observed $^{222}\text{Rn}$ emissions to increase by a factor of ~ 2.5 relative to the mean flux at 3 sites of different soil type when the water table dropped in spring (Fig. 2, Appendix A). Water table depth is generally not an important factor for $^{220}\text{Rn}$ flux however, due to its much shorter diffusion length, and thus $z^d$ (§2.2.2).

Atmospheric pressure
Changes in pressure caused by atmospheric turbulence, the passage of synoptic weather systems, and other mesoscale or synoptic-scale phenomena can affect radon emissions
by forcing atmospheric air into the soil pore space, or inducing mass flow from the soil to the atmosphere. Changes in atmospheric pressure caused by the passage of fronts have been shown to cause significant variations in the $^{222}$Rn emission rate from soils which are porous (dry and sandy) or fractured (Clements and Wilkening, 1974; Schery and Gaeddert, 1982; Duenas and Fernandez, 1987); however, in moist soils diffusion is by far the dominant mechanism of gas transport (§2.2.2), and variations in atmospheric pressure are therefore generally of minor importance (Schery et al., 1982; Schubert and Schulz, 2002).

**Soil temperature**

Many studies have reported a significant correlation between radon flux and soil temperature (e.g. Schery et al., 1989; Dueñas et al., 1997; Koarashi et al., 2000), but for most soils this observed temperature dependence is likely to be due to the fact that changes in soil moisture are closely associated with changes in temperature, rather than to a direct temperature effect (Conen, 2004). An increase in soil temperature will enhance radon emissions because of increased diffusion and thermal expansion of the soil air (which may also occur as a result of localised changes in air pressure, due to changes in partial pressures), and it will also reduce the amount of radon dissolved in the soil water (according to Henry's law, §2.2.1); however, these effects are generally of minor importance over the range of temperatures found in the environment (Schery et al., 1989).

**Freezing of the soil**

The limited number of studies which have included observations of the effect of soil freezing on radon emissions have all reported a marked or total reduction in flux as a result of the soil freezing (Smyth, 1912; Pearson and Jones, 1965; Dörr, 1984 - cited in Feichter and Crutzen, 1990; George, 1981 - cited in Jacob and Prather, 1990). Jacob and Prather (1990) analysed the 3-year time series of $^{222}$Rn flux measurements made by
George (1981) and found $^{222}$Rn emissions to be reduced by a factor of 3 when the soil was frozen compared to when it was not frozen. On the basis of these studies, a substantial reduction or zero radon emissions from frozen soils has generally been assumed in atmospheric studies. Measurements which have been carried out as part of this research demonstrate that freezing (and thus expansion) of the soil water alone will not cause a significant reduction in flux, however, and it is concluded that freezing of the soil is only likely to cause a substantial reduction in emissions when this is accompanied by the formation of a continuous ice layer at the surface, or ice lenses within the soil profile (Chapter 4).

**Snow cover**

Experimental data concerning the effects of snow cover on radon emissions are also limited. On the basis of a small number of observations e.g. Dörr (1984 - cited in Feichter and Crutzen, 1990), who found that a snow cover of 15 cm reduced $^{222}$Rn emissions by 30-40%, a very low or zero emission rate is generally assumed in atmospheric studies. However, Moriizumi et al. have observed atmospheric $^{222}$Rn concentrations to increase to high levels within the nocturnal boundary layer during times of snow cover (Moriizumi et al., 2004), and found that a snow cover of 40-60 cm had no effect on the $^{222}$Rn flux measured indirectly from atmospheric $^{222}$Rn profiles at a site in western Siberia (J. Moriizumi, pers. comm.). Larson (1974) observed large concentrations of $^{222}$Rn above a snow cover of ~ 60 cm, and Kataoka et al. (2003) observed that a snow cover of 20-30 cm depth had no effect on $^{222}$Rn concentrations, but did note a reduction in $^{212}$Pb concentrations (and therefore the $^{220}$Rn flux). Measurements carried out as part of this research found a snow cover of 4-6 cm to have no effect on $^{222}$Rn concentrations, but, a reduction in $^{220}$Rn flux was noted when the snow surface became icy (Chapter 4). Thus, it is concluded that the extent to which a snow cover will affect radon emissions will depend on the physical characteristics.
(porosity and tortuosity) of the snow, and the degree of waterlogging of the soil caused by snow melt. The depth of the snow will also be important for $^{220}$Rn (Chapter 4).

2.3.2 Spatial factors

Radium content of the soil

The radium content of the soil is the most important factor controlling the spatial distribution of radon emissions on the regional scale (Keller and Schütz, 1988; Hafez et al., 1991; Nielson et al., 1996; Dueñas et al., 1997; Ielsch et al., 2001). As the geochemistry of the soil is largely determined by the parent material (Rawlins et al., 2003; Goovaerts and Webster, 1994), there may be considerable variability in the $^{226}$Ra and $^{224}$Ra content of soils areas of complex geology (e.g. Anagnostakis et al., 1996). Mean soil $^{226}$Ra contents typically range from negligible amounts in soils with a high organic content (i.e. peat) to $\sim 300$ Bq kg$^{-1}$ on soils developed from parent material with a high $^{238}$U content, such as granites, black shales, or phosphatic sedimentary rocks (Anagnostakis et al., 1996; McAulay and Marsh, 1992; Myrick et al., 1983). Values much higher than this can be found locally in areas of uranium mineralization, however (Dowdall and O'Dea, 2002).

Soil texture

For soils of a similar radium content, the particle size distribution, or soil texture, is the most important factor causing spatial variations in radon emissions (Dörr and Münnich, 1990). Because of the larger specific surface area of individual soil particles, finer soils tend to have a larger emanating fraction than coarser soils, and thus larger radon fluxes (e.g. Damkjaer and Korsbech, 1985). However, as finer-textured soils tend to have higher soil moisture levels, this effect can be offset by reduced diffusion coefficients (§2.2.2).
Soil thickness

Shallow soils will release less radon than deeper soils of a similar radium content and texture because the reservoir of radium producing radon is smaller. However, soil depth is not an important factor where the soil depth is greater than $z^d$, the relaxation depth of radon (§2.2.2), and, in some cases the water table depth ($z^w$) may be the determining factor (where $z^w > z^d$). Because of its short diffusion length, soil thickness is not an important factor for $^{220}$Rn emissions.

Vegetation

In general, the presence of vegetation will only affect radon emissions indirectly, as a result of its effect on the structure and moisture content of the soil, and water table depth (Schery et al., 1984; Feige and Wiegand, 1998; Schery et al., 1989). Also, due to the increased diffusion length, a closed vegetative cover will generally reduce $^{220}$Rn emissions (Ikebe and Shimo, 1972; Schery et al., 1989), but this is not important for $^{222}$Rn because of its much longer half-life. However, radon emissions may be enhanced directly via transpiration in some circumstances, for example in the case of water-saturated soils (Hinton and Whicker, 1985; Schery, 1989). It is also possible that radon emissions may be enhanced in the vicinity of plants which concentrate radium, such as the Brazil nut tree, in which radium has been found at concentrations up to 200 times greater than in the soil (Smith, 1971).

2.4 Measuring radon emissions from soils

There are a number of different approaches and a wide range of instrumentation available for both detecting radon and measuring its emission rate. The various methods which have been used to measure radon fluxes from soils are described below. Whilst radon detectors are generally calibrated to international standards, methods for measuring radon fluxes currently are not. International intercomparisons of direct measurement techniques (i.e. accumulator methods) have found coefficients of variation
of 34% (Hutter and Knutson, 1998) and 43% (Neznal and Neznal, 2002) for \(^{222}\text{Rn}\) flux measurements, and there has been no comparison of \(^{220}\text{Rn}\) flux measurement techniques to date. Variability between different measurement techniques is therefore a confounding variable when interrelating radon flux measurements, and an issue which needs to be addressed.

### 2.4.1 Methods of detecting radon

Direct methods of detecting radon make use of the fact that it is the only natural gas which emits alpha particles, which cause intense ionisation or molecular excitation in the substances through which they pass. The ionisation process can be detected electronically (e.g. with ionization chambers, semiconductor detectors); by the emission of light pulses (scintillation counting); or by counting the tracks that alpha particles leave in certain substances. Indirect methods of measuring radon involve measuring the activity of radon decay products. Each of these methods is described briefly below (Smith, 1991; Appleton and Ball, 1995). By far the most sensitive and widely used method is zinc-sulphide scintillation counting. An in-depth appraisal of the various methods available for measuring radon is considered outwith the scope of this thesis. Some discussion of the advantages and disadvantages of the different methods and instrumentation for measuring radon can be found in the review of methods for and instrumentation for measuring \(^{222}\text{Rn}\), \(^{220}\text{Rn}\) and their decay products by George et al. (1998).

**Scintillation counting**

When an alpha particle interacts with one of a small number of substances known as scintillators, photons are emitted in the visible part of the spectrum. This pulse of light, or 'scintillation', is then counted using a photomultiplier and suitable counting circuitry (the intensity of light pulses being proportional to the energy absorbed by the scintillator) (Smith, 1991).
Solid state counting. The techniques based on counting pulses from silver-activated zinc sulphide scintillator (Lucas, 1957) are by far the most sensitive for detecting radon, and thus are among the most widely used. Scintillation or 'Lucas' cells vary in size from ~ 0.1 to 3 L, and can be used for continuously monitoring radon concentrations, as well as measuring the radon activity of air samples, or 'grab-sampling'. Radon concentrations are determined from the known half-lives and theoretical build-up of decay products, or via alpha spectrometry.

Liquid scintillation counting. Liquid scintillation counting involves the use of an organic scintillant compound, which is dissolved in an organic solvent, such as xylene or toluene. Many liquid scintillators are efficient extractors of radon from gas or liquid phases.

Gas ionisation chambers
A gas ionisation detector consists of two electrodes contained in a gas-filled chamber with a high electric potential maintained between them. When ionization of the gas occurs, electrons and positive ions are produced, which are driven to the anode and cathode respectively. The resulting electric pulse is recorded and the radon activity is then determined from the number of pulses recorded per unit time.

Semiconductor detectors
Semiconductor detectors can be regarded as the solid-state equivalents of gas ionization detectors. When alpha particles interact with the semiconductor they produce a pulse which is proportional to the energy of radiation. If a suitable multi-channel analyser is used, semiconductor detectors can also be used to identity the nuclide(s) present, as well as measure the activity. Because of the lack of penetration of alpha particles, silicon-gold, lithium-drifted silicon and ion-implanted high-purity detectors are adequate for radon and radon daughter measurements.
Nuclear track detectors

Alpha particles leave marks or 'tracks' in certain materials, for example plastics such as cellulose nitrate and polyallyl diglycol carbonate (also known by the trade name CR-39). The alpha particle tracks are enlarged chemically or electrically, and then the track density is counted, either by point counting, photomicrograph registration, or automatic image analysis techniques. Nuclear track detectors with a diffusion barrier are used to discriminate between $^{222}\text{Rn}$ and $^{220}\text{Rn}$ (Doi et al., 1992).

Counting of decay products

Radon concentrations can also be determined by measuring the activity of their decay products. Methods which are used to continuously monitor radon concentrations in the atmosphere can be described as 'one-filter' (Wilkening, 1959; Lambert et al., 1970) or 'two-filter' methods (Thomas and LeClare, 1970; Hutter et al., 1995; Iida et al., 1991; Whittlestone and Zahorowski, 1998).

One-filter method. Aerosols (essentially fine dust particles), to which polonium almost instantly becomes irreversibly attached, are collected on a filter via an air pump, usually over 30-60 min integration periods. The $^{222}\text{Rn}$ and/or $^{220}\text{Rn}$ decay product activity of the filter is then determined by either alpha or beta counting, or gamma spectrometry (Lambert et al., 1970; Polian et al., 1996; Levin et al., 2002). 'Equilibrium equivalent' $^{222}\text{Rn}$ and $^{220}\text{Rn}$ concentrations are then calculated, by assuming secular equilibrium between radon and its daughters, or by establishing the degree of disequilibrium relative to the ambient radon concentration. The major limitation of this method is that this factor can vary substantially from site to site and with time e.g. due to rainfall.

Two-filter method. Aerosols and ambient (i.e. unattached) $^{222}\text{Rn}$ and $^{220}\text{Rn}$ daughters are filtered out of the sample air, so that only the gas enters the detection cell. $^{222}\text{Rn}$ concentrations are then determined from the activity of newly produced radon decay
products, which are collected on the second filter. The decay product activity is then counted using a zinc sulphide scintillator and photomultiplier. The second filter may be in the form of filter tape or a wire mesh (e.g. Whittlestone and Zahorowski, 1998), but electrostatic deposition has also been used (Iida et al., 1991).

**Use of absorbers**
Absorbers of various kinds e.g. activated charcoal, silica gel, charged metal plates, can be used to concentrate radon and/or its decay products. Radon/decay product concentrations are then determined by a suitable method, for example gamma spectrometry or liquid scintillation counting. Pre-concentration may be necessary when measuring very small concentrations, for example at high levels in the atmosphere, or when trying to detect very small differences in radon concentrations.

### 2.4.2 Methods of measuring radon fluxes
#### 2.4.2.1 Accumulator methods
Accumulator methods involve the interception of the gas flux between the soil and the atmosphere by an inverted container or ‘chamber’ placed over the soil. Depending on the approach taken, chamber methods can be described as either ‘static’ (or closed) or ‘dynamic’ (or open) (Smith and Conen, 2004). In a closed system there is usually a linear increase in gas concentrations, and this permits the flux to be calculated from the observed concentration change over time, the average chamber height, and the gas density. In a dynamic system, air is continuously flushed through the chamber and the concentration differences between the incoming and outgoing air are measured. The flux is then a function of the concentration difference between in-flowing and out-flowing air, the flow rate, chamber area, and gas density. Each approach has its advantages and disadvantages. Whilst the static method permits the detection of very small fluxes, it can significantly underestimate the undisturbed flux as covering the soil alters the natural concentration gradient in the soil (Denmead, 1979; Conen and Smith,
2000; Rayment, 2000). However, static chambers have the considerable advantage that they are much easier to deploy in the field than dynamic chambers, as they do not require an electricity supply and air pumps. Further, the problem of an altered diffusion gradient is only a significant problem for soils of a high porosity, and the risk of this occurring can be minimised with careful chamber design (Conen and Smith, 2000). Another disadvantage with the dynamic method is that it is crucial to maintain as little pressure difference (< 0.2 Pa) to the outside atmosphere as possible in order to avoid inducing mass flow (Fang and Moncrieff, 1998).

$^{222}$Rn and $^{220}$Rn fluxes have been measured using both the static and dynamic chambers, but the static method is the most widely used. For static chamber measurements radon detection by zinc-sulphide scintillation counting has been the most commonly used method, either by grab sampling (e.g. Iida et al., 1996; Somashekarappa et al., 1996; Dueñas et al., 1997) or continuous monitoring (e.g. Saegusa et al., 1996; Ishimori et al., 1998); however, with recent advances in ionisation chamber technology, ionisation chambers are now increasingly being used (e.g. Koarashi et al., 2000; Ferry et al., 2001; Lehmann et al., 1999, 2004; Conen and Robertson, 2002; Martens et al., 2004). Activated charcoal (Pearson and Jones, 1965; Megumi and Mamuro, 1973; Nielson et al, 1996) and solid state nuclear track detectors (Hafez et al. 1991; Evangelista and Pereira, 2002) have also been used in combination with closed chambers. With the dynamic chamber method, zinc-sulphide counting is the favoured approach, due to its greater sensitivity (Schery et al., 1984; Schery et al., 1989; Zahorowski and Whittlestone, 1996).

**Atmospheric profile method**

Indirect estimates of radon flux may be obtained by integrating atmospheric profiles and assuming a steady-state between flux and decay (e.g. Servant, 1964 - cited in Wilkening et al., 1975; Kirichenko, 1970; Anderson and Larson, 1974; Wilkening et al., 1975). Estimates made in this way have the advantage of integrating over larger areas;
however, in the case of $^{222}\text{Rn}$, the assumption of a steady-state between flux and decay is only valid if air masses have been in contact with the land surface for at least 10 days (Turekian et al., 1977). Thus, the situations in which it is applicable are highly dependent on the speed of movement of the air mass.

$^{210}\text{Pb}$ flux method

Large-scale estimates of $^{222}\text{Rn}$ flux can also be deduced from $^{210}\text{Pb}$ deposition fluxes (Turekian et al., 1997; Conen and Robertson, 2002). Estimates made in this way are based on several assumptions, however (Conen and Robertson, 2002/Appendix A).

Boundary layer budget methods

A small number of studies have included regional-scale estimates of $^{222}\text{Rn}$ flux made by boundary-layer budget methods. For example, considering trajectories from the North Sea to Heidelberg, Dörr et al. (1983) estimated the $^{222}\text{Rn}$ flux for the region using $^{222}\text{Rn}$ concentrations monitored at Heidelberg in Germany (assuming negligible $^{222}\text{Rn}$ concentrations before contact with the land), and Kataoka et al. (1992) estimated the regional $^{222}\text{Rn}$ flux from the observed increase in concentrations over time during a surface-based inversion. For valid estimates, however, accurate estimates of the boundary layer height are essential for this method, and these are expensive to obtain (Moncrieff, 2004).

Soil profile methods

$^{222}\text{Rn}$ and $^{220}\text{Rn}$ fluxes have been estimated using diffusion theory and the concentration profile in soil gas (Dörr et al., 1983; Dörr and Münich, 1990; Dueñas et al., 1997), and $^{210}\text{Pb}$ concentrations have been used to provide an estimate of the time-averaged radon diffusion gradient (Schery et al., 1984). Graustein and Turekian (1990) calculated $^{222}\text{Rn}$ fluxes from the soil on the basis of the deficit of $^{210}\text{Pb}$ relative to $^{226}\text{Ra}$ in surface soils.
2.5 Radon flux studies

2.5.1 Range of fluxes and estimates of the global mean flux

Worldwide information on radon flux measurements has been summarised in Wilkening et al. (1975), Turekian et al. (1977), and UNSCEAR (1982), and direct measurements from natural soils since Turekian et al. (1977) have been summarised by Conen and Robertson (2002). Average $^{222}\text{Rn}$ fluxes reported in the literature for different soil types range from $< 1 \text{ Bq m}^{-2} \text{ h}^{-1}$ from waterlogged peat soils (Conen and Robertson, 2002) and poorly developed rocky soils (Whittlestone et al., 1996), to $\sim 220 \text{ Bq m}^{-2} \text{ h}^{-1}$, measured from soils developed on granite bedrock in France (Ielsch et al., 2001). Individual fluxes in excess of $1.8 \times 10^5 \text{ Bq m}^{-2} \text{ h}^{-1}$ have been recorded on soils developed on granite bedrock (Robé et al., 1992). Average $^{220}\text{Rn}$ fluxes reported for specific areas range from $72 \text{ Bq m}^{-2} \text{ h}^{-1}$ (Whittlestone et al., 1996) to $\sim 7200 \text{ Bq m}^{-2} \text{ h}^{-1}$ (Lehmann et al., 1999). Schery et al. (1989) reported individual $^{220}\text{Rn}$ fluxes $> 50,000 \text{ Bq m}^{-2} \text{ h}^{-1}$. Estimates of the global mean $^{222}\text{Rn}$ flux from the land surface based on indirect flux measurements range from $0.7 \text{ atom cm}^{-2} \text{ s}^{-1}$ ($\sim 53 \text{ Bq m}^{-2} \text{ h}^{-1}$) to $1.3 \text{ atom cm}^{-2} \text{ s}^{-1}$ ($\sim 98 \text{ Bq m}^{-2} \text{ h}^{-1}$) (Wilkening et al., 1975; Turekian et al., 1977; Lambert et al., 1982). Due to the limited amount of measurements the world average $^{220}\text{Rn}$ flux is poorly determined, but Schery et al. (1989) suggested that the global mean probably lies somewhere in the range of $\sim 3200$-6800 Bq m$^{-2}$ h$^{-1}$.

2.5.2 Temporal studies

A large number of studies have investigated the influence of meteorological conditions on $^{222}\text{Rn}$ emissions on the day-to-day timescale (e.g. Pearson and Jones, 1965; Megumi and Mamuro, 1973; Dueñas et al., 1997; Kojima, 1998; Koarashi et al., 2000; Ferry et al., 2001), but similar studies for $^{220}\text{Rn}$ have been scarce (Guedalia et al., 1970; Megumi and Mamuro, 1973; Schery et al., 1984). Variations in the soil moisture content due to wetting and drying of the soil after rainfall are the most important cause of variations in radon flux on this time scale (Ussler et al., 1994; Ferry et al., 2001), and are more
important for $^{220}\text{Rn}$ because of its much shorter half-life and therefore diffusion length (§2.3.1). Studies of the temporal variability in radon emissions on the seasonal time-scale have been limited for both $^{222}\text{Rn}$ and $^{220}\text{Rn}$ (Pearson and Jones, 1965; Megumi and Mamuro, 1973; Schübler, 1996; Whittlestone et al., 1998). Seasonal variations of a factor of two have been reported for $^{222}\text{Rn}$ (Schübler, 1996; Whittlestone et al., 1996) and a factor of three for $^{220}\text{Rn}$ (Whittlestone et al., 1998). Changes in water table depth and soil moisture content are important factors for $^{222}\text{Rn}$ but water table depth is unlikely to be an important factor for $^{220}\text{Rn}$ on the seasonal time-scale, because of its much shorter diffusion length (§2.3.1). Schübler (1996) noted the amplitude of the seasonal cycle in $^{222}\text{Rn}$ emissions to depend on the texture of the soil, with finer-textured soils tending to have a greater amplitude in seasonality.

The temporal variability of $^{222}\text{Rn}$ emissions has also been investigated on the diurnal time-scale (e.g. Guedalia et al., 1970; Schery et al. 1984; Ishimori et al., 1998; Kojima, 1998; Ferry et al., 2001). Kojima (1998) found a diurnal trend in $^{222}\text{Rn}$ flux of typically 20%, with emissions peaking in the afternoon, in correspondence with the minimum in the difference between the pressure at the soil surface and at 1 m depth. This trend in emissions was also observed by Schery et al. (1984), who, for a gravelly sandy loam soil, found $^{222}\text{Rn}$ emissions to increase by a factor of 1.5 to 2. Ishimori et al. (1998) and Ferry et al., (2001), on the other hand, found no diurnal trend in emissions. As advective transport is generally not an important process for gas transport in soils (§2.2.2), a diurnal trend in emissions due to the typical diurnal pattern in atmospheric pressure and temperature is unlikely to occur, except in highly porous or fractured soils (Schery et al., 1984; Chapter 4). Likewise, thermal gradients in the soil, which have been reported to be the cause of diurnal variations in radon emissions (Guedalia et al., 1970), are generally unlikely to be important (Schery and Petschek, 1983).
2.5.3 Spatial studies

Systematic surveys of $^{222}_{\text{Rn}}$ flux on the regional-scale have been fairly limited (Schery et al., 1989; Graustein and Turekian, 1990; Whittlestone et al., 1996, 1998; Nielson et al., 1996; Jennings, 2003), and there have been even fewer for $^{220}_{\text{Rn}}$ (Schery et al., 1989; Whittlestone et al., 1996, 1998). The only investigation to have applied any geostatistical analysis appears to be that conducted by Nielson et al. (1996), for the state of Florida, USA. They found an approximate doubling of the geometric standard deviation in $^{222}_{\text{Rn}}$ flux when increasing from an area of 1 m$^2$ to 34 km$^2$, and that this relation held over 12 orders of magnitude. $^{222}_{\text{Rn}}$ and $^{220}_{\text{Rn}}$ fluxes are found to have an approximately log-normal distribution on the regional scale (Schery et al., 1989; Nielson et al., 1996), and to be strongly related to the radium content of the soil (§1.4.2). On the global-scale, trends in $^{222}_{\text{Rn}}$ emissions have been investigated by Conen and Robertson (2002), who investigated the spatial distribution of radon flux measurements published in the literature (Chapter 5 / Appendix A). They found a trend of decreasing $^{222}_{\text{Rn}}$ emissions with increasing latitude in the Northern Hemisphere, and attributed this to the increasing proportion of wetlands at higher latitudes.

2.5.4 Modelling studies

A small number of studies have attempted to model the spatial distribution of $^{222}_{\text{Rn}}$ emissions on regional-scales. Eckhardt (1990 - cited in Chevillard et al., 2002) produced a $^{222}_{\text{Rn}}$ flux map of Europe based on the Food and Agriculture Organisation (FAO) soils map of the world and spot measurements of $^{222}_{\text{Rn}}$ flux from various soil types around Europe. Predicted fluxes ranged from 0.3 to 1.5 atom cm$^{-2}$ s$^{-1}$ (≈ 23 to 113 Bq m$^{-2}$ h$^{-1}$) and the mean $^{222}_{\text{Rn}}$ flux was 0.8 atom cm$^{-2}$ s$^{-1}$ (cited in Biraud et al., 2002), which is equivalent to ~ 65 Bq m$^{-2}$ h$^{-1}$. Using a similar approach, Nielson et al. (1995 - cited in Nielson et al., 1996) produced a $^{222}_{\text{Rn}}$ flux map for the state of Florida, USA. Sakashita et al. (1997) produced a $^{222}_{\text{Rn}}$ flux map for the central 200 x 200 km area of Nagoya, Japan, by weighted interpolation between flux measurements made in the
region, and Ielsch et al. (2002) have proposed a method for predicting \(^{222}\text{Rn}\) flux on a regional scale, based on rock and soil chemical and physical properties and a diffusion-theory \(^{222}\text{Rn}\) transport model. The only attempt to produce a global \(^{222}\text{Rn}\) emissions map is that of Schery and Wasiolek (1998), who produced a \(^{222}\text{Rn}\) emissions map with a 1° by 1° resolution. The map was produced using \(^{226}\text{Ra}\), soil moisture and temperature data, using a model which was based on porous media transport theory, and was calibrated with \(^{222}\text{Rn}\) flux data from Australia and Hawaii (Schery et al., 1989; Whittlestone et al., 1996). The model predicted a global mean flux of 1.6 atom cm\(^{-2}\) s\(^{-1}\) (~120 Bq m\(^{-2}\) h\(^{-1}\)), which is about 20% greater than the highest global mean estimate of 1.3 atom cm\(^{-2}\) s\(^{-1}\) (§2.5.1), and that regional variations in emissions of a factor of three, and seasonal variations of a factor of two, would not be uncommon. Because of the limited amount of \(^{222}\text{Rn}\) flux data and information on the relevant soil parameters required for modelling \(^{222}\text{Rn}\) emissions, these models are generally very crude and can only be considered as a first (but nevertheless very useful) step towards providing a reasonably accurate spatial description of \(^{222}\text{Rn}\) emissions, and should therefore be interpreted with caution.

2.6 Atmospheric applications of \(^{222}\text{Rn}\) and \(^{220}\text{Rn}\)

The first studies relating atmospheric activities of \(^{222}\text{Rn}\) and \(^{220}\text{Rn}\) to the transport properties of the atmosphere were made in the early part of the last century (e.g. Hess and Schmidt, 1918; Schmidt, 1926 - cited in Ikebe and Shimo, 1972), not long after their discovery by Ernest Rutherford in 1899 (\(^{220}\text{Rn}\)), and Fredrich Ernst Dorn in 1900 (\(^{222}\text{Rn}\)). However, it was not until the late 1950s, with the development of new measurement techniques (the ‘Lucas’ cell - §2.4.1), that radon was first used in more quantitative studies, or as a ‘tracer’ of atmospheric transport processes, an application first proposed by Israël (1951). The first tracer studies were concerned with estimating turbulent diffusion coefficients from atmospheric profiles of \(^{222}\text{Rn}\) and \(^{220}\text{Rn}\) activities (e.g. Wilkening, 1959; Jacobi and André, 1963). About ten years later \(^{222}\text{Rn}\) was first-
used as a tracer of long-range advective transport in studies of atmospheric circulation (Lambert et al., 1970; Wilkness et al., 1974). The first studies to apply $^{222}\text{Rn}$ to the estimation of surface-atmosphere fluxes of other trace gases, and to assess horizontal and vertical transport in atmospheric transport models were carried out in the 1980s (Dörr et al., 1983; Brost and Chatfield, 1989). Along with the global network of $^{222}\text{Rn}$ monitoring stations, these two applications have grown substantially over the last decade or so (Zahorowski et al., 2004b).

2.6.1 Studies relating to the turbulent diffusivity of the lower troposphere

$^{222}\text{Rn}$ and $^{220}\text{Rn}$ have been used extensively to calculate vertical, or eddy, diffusion coefficients for the lower atmosphere (e.g. Wilkening, 1959; Jacobi and André, 1963; Brot et al., 1970; Ikebe and Shimo, 1972; Porstendörfer et al., 1991; Butterweck et al., 1994; Doi and Kobayashi, 1994; Lee and Larson, 1997; Lehmann et al., 1999). As the vertical gradient of activity concentrations is a function of turbulent exchange and the half-life of the radon isotope, if the surface atmosphere flux of $^{222}\text{Rn}$ or $^{220}\text{Rn}$ is known, the eddy diffusivity, $K$, can be calculated from vertical profiles of activity concentrations (Butterweck et al., 1994). One of the major advantages of this method over most other methods used for estimating the vertical eddy diffusivity is that it can be used in conditions where most micrometeorological methods (e.g. aerodynamic methods or the Bowen-ratio method) fail, as conventional models of atmospheric dispersion are no longer applicable under these conditions, e.g. inside crops and during nocturnal inversions (Butterweck et al., 1994; Mahrt, 1998). More sophisticated approaches such as the eddy covariance method (e.g. Moncrieff et al., 1997; Soegaard et al., 2003) involve large experimental effort.

Other applications of radon concerned with the mixing properties of the lower atmosphere include using $^{222}\text{Rn}$ as an indicator of the vertical stability of the lower atmosphere, by relating activity concentrations to Pasquill's and Turner's stability
indexes (e.g. Guedalia, 1980; Fujinami and Esaka, 1987; Dueñas et al., 1996), and estimating the depth of convective and nocturnal boundary layers by examining diurnal variations in atmospheric concentrations at more than one depth (Fujinami and Esaka, 1988; Kataoka et al., 1998; Sesana et al., 2003). Kataoka et al. (2003) used continuous observations of $^{222}$Rn, its short-lived daughters, and $^{212}$Pb, at three sites in Kamisaibara Village, Japan, to investigate the meteorology of complex terrain (drainage winds in particular), and Cuculeanu and Lupu (2001) have used a combination of $^{222}$Rn and $^{220}$Rn decay products to investigate more fundamental aspects of atmospheric transport.

2.6.2 Identifying the origin of air masses

As radon emissions from the oceans are at least two orders of magnitude smaller than those from the land (Wilkening and Clements, 1975; Zaborowski et al., 2004a), radon isotopes can be used to distinguish between continental and maritime air masses on the basis of their relatively high and low radon concentrations (e.g. Brunke et al., 2004). $^{222}$Rn has been widely used in this context, as a means of identifying the origin of air masses, and estimating the extent of air mass contact with the land (e.g. Lambert et al., 1970; Wilkness et al., 1974; Polian et al., 1986; Kritz et al., 1990; Balanski and Jacob, 1990; Carvalho, 1995). As $^{222}$Rn concentrations are sensitive to fast, short-lived changes in flow, they are more useful than trajectory calculations alone, because most trajectory models are not sensitive to short-duration sub-synoptic meteorological events (Hansen et al., 1990). Because the mean atmospheric lifetime of $^{222}$Rn is comparable to the lifetimes of short-lived atmospheric pollutants such as NOx, SO2, CO, and O3, and the residence times of water and aerosols, correlation of these substances with $^{222}$Rn activity can be used to identify their sources (e.g. Larson et al., 1972; Prospero and Carlson, 1970; Wyputta, 1997; Zauker et al., 1996; Sakashita et al., 2004). $^{220}$Rn and its decay product $^{212}$Pb have been used as a tracers of landmass contact on the local scale (e.g. Polian et al., 1986; Whittlestone et al., 1992).
2.6.3 Measurement of trace gas fluxes

$^{222}$Rn has been widely used as a reference gas in estimating fluxes of other surface-emitted trace gases, such as CO$_2$, N$_2$O and CH$_4$. The tracer method of measuring gas fluxes works on the principle of scaling the unknown emissions of a target gas (e.g. CO$_2$) to the assumed or well-determined source of a reference tracer – in this case $^{222}$Rn. The flux of the target gas $J_x$ is calculated from:

$$J_x = \frac{\Delta C_x}{\Delta A_{Rn-222}} J_{Rn-222}$$  \hspace{1cm} (2.5)

where $\Delta C_x$ and $\Delta A_{Rn-222}$ are the concentration differences of the target gas and $^{222}$Rn in the atmosphere, and $J_{Rn-222}$ is the $^{222}$Rn flux. It is assumed that all gases are transported in the atmosphere with equal efficiency by turbulent processes.

$\Delta C_x$ and $\Delta A_{Rn-222}$ may be derived from concentration changes over time occurring as a result of accumulation in the boundary layer during a synoptic event (e.g. Dörr and Münich, 1990; Gaudry et al., 1990; Schmidt et al., 1996; Moriiizumi et al., 1996; Wilson et al., 1997; Kuhlmann et al., 1998; Levin et al., 1999; Biraud et al., 2000; Conen et al., 2002), or during nocturnal inversions (Conen et al., 2002). This approach gives a flux estimate which is representative of the flux on the regional-scale ($10^2$ to $10^5$ km$^2$), and offers a much cheaper alternative to other techniques available for estimating fluxes on this scale. Boundary layer budget methods (e.g. Denmead et al., 1996; Levy et al., 1999) require accurate estimates of the boundary layer height, which are expensive to obtain (e.g. radiosondes, acoustic sounding, profiles of atmospheric constituents measured from aircraft). Eddy covariance measurements made from aircraft (e.g. Gioli et al., 2004) are also expensive. As the $^{222}$Rn-tracer method does not require the boundary layer height (by scaling the flux of the gas of interest to that of $^{222}$Rn the
boundary layer height is no longer required — Eq. 2.5), it provides a much cheaper alternative to these other methods. However, as the error in the estimate of the target gas is directly proportional to the error in the $^{222}$Rn source term used (Eq. 2.5), the accuracy of $^{222}$Rn-based flux estimates are directly dependent on the accuracy of the $^{222}$Rn source term used. Whilst some workers have used reasonably well-characterised source terms in these studies i.e. have taken into account some of the spatial and temporal variability in emissions, in some studies the $^{222}$Rn source term used has been a mean value based on only a few measurements, or an estimate of the regional mean $^{222}$Rn based on modeling studies. In the latter case, these flux estimates should be interpreted with caution.

$\Delta A_{^{222}Rn}$ can also be a concentration difference observed between two heights. Used in this way, the method gives an estimate which is representative of emissions on the on local scale (0.1 to 10 ha). A small number of studies have estimated the net $CO_2$ exchange between forest canopies and the atmosphere by using this method (Trumbore et al., 1990; Ussler et al., 1994; Martens et al., 2004), and Conen et al., (2002) have estimated $N_2O$ fluxes from grasslands by integrating over both height and time, thus providing flux estimates for two different scales at the same time. Used in this way, the $^{222}$Rn tracer method is particularly useful as it can be used under light wind or stable conditions, when most micrometeorological methods (e.g. aerodynamic methods or the Bowen-ratio method) are not valid, as conventional models of atmospheric dispersion are no longer applicable under these conditions (Butterweck et al., 1994; Mahrt, 1998). More sophisticated approaches to measuring trace gas fluxes at this scale, such as the eddy covariance method (e.g. Moncrieff et al., 1997; Soegaard et al., 2003) involve large experimental effort, and have large analysis requirements. The radon method is also attractive in that it can easily be automated, and it permits the calculation of smaller fluxes on the field scale; these fluxes (e.g. $N_2O$ and $CH_4$) cannot be readily detected using micrometeorological methods, except for when complex tunable diode laser
systems are used. Further, there are particular environments in which the $^{222}\text{Rn}$ tracer method could be exploited to provide a much better understanding of trace gas budgets for that ecosystem. One example is the under-canopy of forests (e.g. Martens et al., 2004), where conventional models of atmospheric dispersion, and thus micrometeorological methods, are generally not applicable. Another is in regions where termites produce large and very localised emissions of CH$_4$ in an area which is otherwise a CH$_4$ sink (e.g. MacDonald et al., 1998). As it is difficult to measure CH$_4$ emissions by chambers in this situation, the $^{222}\text{Rn}$ tracer method could prove to be extremely useful (but this does not appear to have been attempted).

Trace gas fluxes have also been calculated using $^{222}\text{Rn}$ and $^{220}\text{Rn}$-derived vertical diffusion coefficients (e.g. Butterweck et al., 1994), $^{220}\text{Rn}$-derived aerodynamic resistances, and $^{222}\text{Rn}$-derived soil diffusivities (e.g. Dörr and Münnich, 1987; Uchida et al., 1997; Dueñas et al., 1999).

2.6.4 Evaluation and parameterisation of atmospheric transport models

$^{222}\text{Rn}$ is routinely used to validate and intercompare atmospheric transport models by means of comparing modelled concentrations with atmospheric observations (e.g. Feichter and Crutzen, 1990; Genthon and Armengaud, 1995; Lin et al., 1996; Jacob et al., 1997; Stevenson et al., 1998; Dentener et al., 1999; Rasch et al., 2000; Taguchi et al., 2002; Gupta et al., 2004; Sakashita et al., 1997; Chevillard et al., 2002). In this context, $^{222}\text{Rn}$ is particularly useful as a tracer of sub-scale convective and synoptic transport processes, and the long-range transport of continental air masses. Vertical profiles of $^{222}\text{Rn}$ concentrations are also used to parameterise convection in models (e.g. Collins et al., 2002). Current practice is to assume a spatially homogeneous and constant $^{222}\text{Rn}$ emission rate or ‘source-term’ of 1 atom cm$^{-2}$ s$^{-1}$ from all ice-free land surfaces, and zero emissions from the oceans; however, it is generally acknowledged that this undifferentiated source term is limiting model validations and parameterisations. Some
modellers have modified the 1 atom cm^{-2} s^{-1} source term so as to take into account some of the variability in Rn emissions, for example, Lee and Feichter (1995) assumed a reduced source strength of 0.005 atom cm^{-2} s^{-1} between 60°N and 70°N (to account for apparent snow cover and soil freezing effects), and found that this improved model predictions of Pb deposition rates. Other modifications of the Rn source term which have been used include accounting for a small oceanic flux (Heimann et al., 1990; Taguchi et al., 2002); increasing emissions from southeast Asia (Dentener et al., 1999; Taguchi et al., 2002); and taking into account variations in emissions due to soil texture (Dentener et al., 1999; Chevillard et al., 2002) and snow cover (Dentener et al., 1999). Some workers have also attempted to improve Rn predictions by taking temporal variations in Rn emissions into account (Jacob and Prather, 1990; Lin et al., 1996; Gentthon and Armengaud, 1995). In general, these studies which have been concerned with modifying the Rn source term have been of a qualitative nature only, i.e. they have not quantified any improvement in prediction; however, as part of this research, the effect of including a trend of decreasing Rn emissions with increasing latitude in the Northern Hemisphere (as indicated by large-scale indirect Rn flux measurements - Conen and Robertson (2002)/Chapter 5) in the generally-assumed 1 atom cm^{-2} s^{-1} source term has been quantified (Robertson et al., 2005/Appendix B/ Chapter 7). Compared to the spatially uniform 1 atom cm^{-2} s^{-1} source term, the ‘northwards-decreasing’ source term was found to significantly improve the prediction of Rn concentrations by a global chemistry-transport model (STOCHEM-Ed) overall i.e. globally, with the greatest improvement for locations north of 50°N, where the mean prediction/observation ratio was reduced from 2.8 to 0.87.
Chapter 3

Methods

3.1 Introduction

In this chapter the techniques which were used to measure radon fluxes in this study are described. Throughout this research, $^{222}$Rn and $^{220}$Rn fluxes have been measured by the closed (or static) chamber method (§2.5.2), using an AlphaGUARD PQ2000PRO radon monitor (Genitron Instruments, Frankfurt) for radon detection. Other research groups have used the AlphaGUARD in combination with closed chambers to measure $^{222}$Rn fluxes (e.g. Koarashi et al., 2000; Ferry et al., 2001), and Lehmann et al. (1999, 2004) have measured $^{222}$Rn and $^{220}$Rn fluxes simultaneously using two AlphaGUARD instruments joined in series (the first measuring total radon activity ($^{222}$Rn and $^{220}$Rn), and the second measuring $^{222}$Rn activity only). The approach used in this research is novel in that only one AlphaGUARD has been used to measure $^{222}$Rn and $^{220}$Rn fluxes simultaneously (from the same chamber).

First, the theory behind determining $^{222}$Rn and $^{220}$Rn fluxes by the closed chamber method is outlined in §3.2. The instrumentation, equipment and procedures used to measure radon fluxes are then described in §3.3. Two slightly different methods were used: 1) simultaneous measurement of $^{222}$Rn and $^{220}$Rn fluxes by continuously monitoring the increase in total radon activity ($^{222}$Rn and $^{220}$Rn) inside the chamber headspace (from here-on termed the ‘continuous monitoring’ method); and 2) measurement of $^{222}$Rn fluxes by grab-sampling of the chamber headspace air, and subsequent analysis of air samples in the laboratory (from here-on termed the ‘grab-
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Methods

sampling' method). As part of the latter approach, an automated analysis system was developed to enable the measurement of $^{222}\text{Rn}$ flux at more than one location simultaneously, in order to permit replicate measurements and studies of the local-scale spatial variability in which flux measurements are independent of time. As far as is known, this is the first time this has been done. In §3.4, the possible errors associated with static chamber flux measurements are described, and, finally, in §3.5 the results of a comparison of the 'continuous monitoring' method of measuring $^{222}\text{Rn}$ fluxes to two methods used by researchers in Japan are presented and discussed.

3.2 Theory: measuring $^{222}\text{Rn}$ and $^{220}\text{Rn}$ fluxes by the closed chamber method

3.2.1 Growth of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ activities inside a closed chamber

The increase in the $^{222}\text{Rn}$ or $^{220}\text{Rn}$ activities inside a closed chamber can be described by:

$$A_{\text{Rn},t} = \frac{J_{\text{Rn}} S}{V \lambda} (1 - e^{-\lambda t}) + A_{\text{Rn},0}$$

(3.1)

where $A_{\text{Rn},t}$ is the $^{222}\text{Rn}$ or $^{220}\text{Rn}$ activity (Bq m$^{-3}$) inside the chamber at time $t$ (s); $J_{\text{Rn}}$ is the flux of $^{222}\text{Rn}$ or $^{220}\text{Rn}$ into the chamber (Bq m$^{-2}$ s$^{-1}$); $S$ is the surface area covered by the chamber (m$^2$); $V$ is the volume of the chamber (m$^3$); $\lambda$ is the appropriate radioactive decay constant (s$^{-1}$); and $A_{\text{Rn},0}$ is the activity of $^{222}\text{Rn}$ or $^{220}\text{Rn}$ at time $t = 0$ (i.e. the ambient activity at closure). It is assumed that storage of radon in the soil and leakage from the chamber are negligible, and that the air in the chamber headspace is well mixed.

An example of the growth of $^{222}\text{Rn}$ ($A_{\text{Rn},222}$), $^{220}\text{Rn}$ ($A_{\text{Rn},220}$), and total radon ($A_{\text{Rn},222 + \text{Rn},220}$) activities inside a closed chamber is shown in Figure 3.1. Activity values were modelled at 1 s time steps for the first hour of closure, using Eq. (3.1).
Values are for $^{222}$Rn and $^{220}$Rn fluxes of 42 and 1125 Bq m$^{-2}$ h$^{-1}$; initial $^{222}$Rn and $^{220}$Rn concentrations of 10 and 76 Bq m$^{-3}$; and a chamber height of 20 cm. As the half-life of $^{222}$Rn (3.82 days) is long relative to the time shown, the $^{222}$Rn activity increases almost linearly, and thus can be modelled using linear regression. This is not the case for $^{220}$Rn, however, as, due to its very short half-life (56 s), the $^{220}$Rn activity quickly reaches an equilibrium value (Figure 3.1), and therefore cannot be modelled using linear regression. A secular (or radioactive) equilibrium of 99.9% is reached after 9 min 20 s, or 10 half-lives (Kirby, 1954).

![Figure 3.1. Simulated $^{222}$Rn, $^{220}$Rn and total radon ($^{222}$Rn + $^{220}$Rn) activities for the first hour of chamber closure. Activity values are for $^{222}$Rn and $^{220}$Rn fluxes of 42 and 1125 Bq m$^{-2}$ h$^{-1}$, initial $^{222}$Rn and $^{220}$Rn activities of 10 and 76 Bq m$^{-3}$, and a chamber of 20 cm height. Due to its short half-life (56 s), the $^{220}$Rn activity quickly reaches an equilibrium value (99.9% after 9 min 20 s, or 10 half-lives), but $^{222}$Rn activities increase almost linearly because its half-life is relatively long (3.82 days).]
3.2.2 Calculating the $^{222}$Rn flux

Assuming a linear change in activity inside the chamber, the $^{222}$Rn flux, $J_{(\text{Rn}-222)}$, is given by:

$$J_{\text{Rn}-222} = \frac{V}{St} (A_{\text{Rn}-222,t} - A_{\text{Rn}-222,0})$$  \hspace{1cm} (3.2)

where $A_{\text{Rn}-222,t}$ is the $^{222}$Rn activity at time $t$ seconds after closure (the end of the accumulation time); and $A_{\text{Rn}-222,0}$ is the initial, or ambient, $^{222}$Rn activity.

Eq. (3.2) simplifies to:

$$J_{\text{Rn}-222} = m_{\text{Rn}-222} h$$  \hspace{1cm} (3.3)

where $m_{\text{Rn}-222}$ is the gradient of the linear regression of the change in $^{222}$Rn activities with time and $h$ is the chamber height. As the signal measured by the AlphaGUARD is the total radon activity (the instrument does not distinguish between the different isotopes), $m_{\text{Rn}-222}$ is not known unless a delay volume has been used to prevent $^{220}$Rn from entering the radon monitor. However, as the $^{220}$Rn activity reaches equilibrium after ~ 7 min (Figure 3.1), the increase in $A_{(\text{Rn}-222 + \text{Rn}-220)}$ after this point in time is solely due to $^{222}$Rn, and thus $m_{(\text{Rn}-222 + \text{Rn}-220)}$ — the gradient of the linear regression of the change in total radon activity with time — is equal to $m_{\text{Rn}-222}$, and the $^{222}$Rn flux can be calculated by replacing $m_{\text{Rn}-222}$ with $m_{(\text{Rn}-222 + \text{Rn}-220)}$ (after the $^{220}$Rn activity has reached equilibrium) in Eq. (3.3).

Many workers have reported linear increases in $^{222}$Rn activity inside chambers over typical deployment times (1-2 hours), and some for much longer periods, for example, Dörr and Münnich (1990) reported linear increases in $^{222}$Rn for up to 6 hours. In this
research, $^{222}\text{Rn}$ activities were found to increase linearly over typical closure times of 1.5 - 2 hours (Figure 3.2), and also for times much longer than this (Figure 3.3).

![Graph showing the increase in total radon activity](image)

**Figure 3.2.** Examples of the increase in total radon activity ($A(\text{Rn-222} + \text{Rn-220})$) measured inside a closed chamber, after the $^{220}\text{Rn}$ activity had reached equilibrium (i.e. excluding the first 10 min interval). Higher $r^2$ values are generally obtained for larger fluxes due to the improved counting statistics of higher activities (the scatter in the increase in activity mostly being random errors due to counting statistics).

However, as illustrated in Fig. 3.3, due to the progressive decrease in the diffusion gradient between the soil and chamber headspace with closure time, the decay of the accumulated $^{222}\text{Rn}$, and possible leakage of the chamber air to the outside atmosphere, at some time after chamber closure the rate of increase in $^{222}\text{Rn}$ activity begins to decrease. The underestimation of the $^{222}\text{Rn}$ flux as a result of a reduced diffusion gradient between the soil and chamber headspace is illustrated more clearly in Figure 3.4, which shows (for the same data in Fig. 3.3) the gradient of the linear regression ($m_{\text{Rn-222}}$) as a function of time.
Figure 3.3. The increase in $^{222}\text{Rn}$ activity measured inside a closed chamber over a period of two days. After $\sim 400$ min ($\sim 6.5$ hours) the rate of increase begins to decline as a result of the reduced diffusion gradient between the soil and the chamber headspace, the decay of the accumulated $^{222}\text{Rn}$, and possible leakage of the chamber air to the outside atmosphere.

Figure 3.4. The gradient of the linear regression of $^{222}\text{Rn}$ activity as a function of chamber closure time, for the data shown in Fig. 3.3. Consistently lower fluxes were measured after closure times $> 400$ min ($\sim 6.5$ hours).
Some investigators have chosen to model $^{222}\text{Rn}$ fluxes non-linearly because of this effect (e.g. Aldenkamp et al., 1992); however, this is a complex approach, and, if the chamber closure time is kept to a minimum, an altered diffusion gradient is only likely to be a significant problem for soils with a high air-filled porosity (Conen and Smith, 2000; Lehmann et al., 2004). Perturbation of the natural diffusion gradient as a source of error with chamber measurements is discussed in more detail in §3.4.1

3.2.3 Calculating the $^{220}\text{Rn}$ flux

Once the $^{220}\text{Rn}$ activity has reached its equilibrium value (Fig. 3.1), the number of $^{220}\text{Rn}$ atoms entering the chamber per unit time is equal to the number decaying at that particular activity. Thus, if the $^{220}\text{Rn}$ equilibrium activity is known, the $^{220}\text{Rn}$ flux, $J_{^{220}\text{Rn}}$, can be calculated from:

$$
J_{^{220}\text{Rn}} = (E_{^{220}\text{Rn}} - E_{^{220}\text{Rn}} e^{-\lambda t}) h
$$

(3.4)

where $E_{^{220}\text{Rn}}$ is the $^{220}\text{Rn}$ equilibrium activity, $\lambda$ is the $^{220}\text{Rn}$ decay constant (0.012375 s$^{-1}$), $t$ is a short time interval (s), and $h$ is the chamber height. $E_{^{220}\text{Rn}}$ can be derived by subtracting the activity due to $^{222}\text{Rn}$ at time $t_0$ (i.e. the ambient $^{222}\text{Rn}$ activity at chamber closure, $A_{^{222}\text{Rn},t_0}$), from the y-axis intercept of the linear regression through the total radon activity ($^{222}\text{Rn} + ^{220}\text{Rn}$) after the $^{220}\text{Rn}$ activity has reached equilibrium (Figure 3.5).
3.3 Radon flux measurements: instrumentation and methods

3.3.1 AlphaGUARD radon monitor

The AlphaGUARD PQ 2000PRO (Genitron Instruments, Frankfurt) is a high-precision portable radon monitor which uses a pulse ionisation chamber in combination with digital signal processing for radon detection. The instrument detects both $^{222}\text{Rn}$ and $^{220}\text{Rn}$, but does not discriminate between the two isotopes. Thus, the signal given by the instrument is the activity (in units Bequerels per cubic metre) due to both $^{222}\text{Rn}$ and $^{220}\text{Rn}$. The AlphaGUARD also measures atmospheric pressure, air temperature and humidity, and can be operated in two modes: 1) a diffusion mode, in which gas enters the ionisation chamber by diffusion through a glass fibre aerosol filter, or 2) an active or flow mode, in which gas entry is enforced using a pump. For this research, the
AlphaGUARD was used in flow mode only, using the ‘AlphaPUMP’, a small battery-operated pump designed for use with the AlphaGUARD (Figure 3.6). The AlphaPUMP has three possible flow rates: 0.3, 0.5 or 1 L min\(^{-1}\), and the AlphaGUARD has a measuring cycle of either 1 min or 10 min. Air is pumped into and out of the instrument via 4 mm Tygon tubing and adaptor valves, which is attached to the active adaptor valves of the instrument (Fig. 3.6). A small fibre dust filter is used to prevent aerosols (and thus radon decay products) from entering the AlphaGUARD.

**Figure 3.6.** Schematic diagram of the AlphaGUARD and AlphaPUMP in operation in a closed loop with a closed (or static) chamber (after Genitron Instruments, 1998).

The design of the AlphaGUARD ionisation chamber is shown schematically in Figure 3.7. The chamber is cylindrical with a volume of 0.56 L. It has a stainless steel
interior, which has a potential of +750 V when the instrument is switched on, and a stiff centre electrode (which has a potential of 0 V) is located along the longitudinal axis. The electric pulse generated by the deposition of electrons and positive ions to the anode and cathode, respectively, is fed to an amplifier unit, and the worked-up measuring signals are then transmitted to an electronic network for further digital processing.

![Diagram of AlphaGUARD ionisation chamber](image)

**Figure 3.7.** Schematic diagram of the AlphaGUARD ionisation chamber (after Genitron Instruments, 1998).

The reported detection efficiency of the AlphaGUARD's active cell is 1 count min⁻¹ per 20 Bq m⁻³ (Genitron Instruments, 1998). In theory, the ionisation chamber's sensitivity to $^{220}\text{Rn}$ should be the same as for $^{222}\text{Rn}$, but this has not been tested. The lower limit of detection of the AlphaGUARD is 2 Bq m⁻³, and at the time of manufacture the background signal due to internal contamination of the detector was < 1 Bq m⁻³ (Genitron Instruments, 1998). A self-triggering automatic background correction function corrects for the gradual increase in instrument background with time due to the
build-up of $^{210}$Pb inside the ionisation chamber, and this correction factor can be manually fine-tuned if a higher level of precision is required. The AlphaGUARD instrument used in this research has been calibrated for $^{222}$Rn by the manufacturer using certified gas standards to within ± 3% (plus the uncertainty of the primary standard).

Both the AlphaGUARD and AlphaPUMP operate on a 12 V DC supply, or from the mains using an adapter. When fully charged, the internal battery of the AlphaGUARD lasts for a maximum of 10 days. Data are stored in the memory of the monitor for 6 months (or until manually deleted), and can be downloaded to a PC using the AlphaEXPERT software package (Genitron Instruments). In addition to the radon activity data (an activity value and error) and meteorological data (temperature, pressure and humidity), the information available for downloading includes two quality assurance values: one relating to the condition of the hardware, and the other to the quality of the data.

3.3.2 Chambers

Three different designs of closed chamber were used in this research (Figure. 3.8). The most frequently used design was a cylindrical polypropylene chamber of 40 cm diameter and 20 cm in height, with an aluminium lid (Fig. 3.8a). This is essentially the same design of chamber described in Clayton et al. (1994) and Dobbie et al. (1999), except that the lid has two holes rather than one, to enable circulation of air in a closed loop between the chamber and radon monitor (Fig. 3.6). For reasons of portability, a smaller version of this chamber (25 cm diameter and 25 cm height) was sometimes used (Fig. 3.8b). The third design of chamber was a 70 cm by 70 cm and 20 cm-high galvanised steel automatic chamber (Fig. 3.8c). This is the same design as described in Smith and Dobbie (2001), and is described in more detail in Chapter 4.
Figure 3.8. The three designs of closed chamber used: (a) The 40 cm diameter chamber (20 cm high); (b) the 25 cm diameter chamber (25 cm high); and (c) the 70 cm-square automatic chamber (20 cm high).
3.3.3 Measuring $^{222}$Rn and $^{220}$Rn fluxes by the continuous monitoring method

The 'continuous monitoring' method of measuring $^{222}$Rn and $^{220}$Rn fluxes, in which the total radon activity ($A_{\text{Rn-222} + \text{Rn-220}}$) inside the chamber headspace is continuously monitored, was the method used when it was not necessary or possible to carry out replicate measurements (in which case fluxes were measured using the 'grab-sampling' method - §3.3.4).

Analytical system

The typical analytical system for measurement of $^{222}$Rn and $^{220}$Rn fluxes by the continuous monitoring method is shown in Figures 3.7 and 3.8a. The system essentially consists of the AlphaGUARD and AlphaPUMP with their tygon tubes and the aerosol filter (§3.3.1), and a chamber and its lid (§3.3.2). In order to protect the monitor and pump from any rain, the instruments are kept together in a custom-built wooden box (Fig. 3.8a), or a nylon waterproof bag. The tygon tubing is attached to the chamber by two 20 cm-length plastic tubes, which are inserted into holes in the chamber lid. A 25 ml glass beaker with a rubber stopper, through which air is drawn prior to entering the monitor, is used as a water trap, to reduce condensation in the tubing. If the $^{220}$Rn flux is being measured, a 12 L Tedlar® bag is used to collect an ambient air sample, which is later analysed in the laboratory (in order to obtain the ambient $^{222}$Rn activity at closure, $A_{\text{Rn-222},0}$ - §3.2.2). A small fan attached to a 12 V battery, and supported on four short sticks pushed into the soil in the middle of the chamber, is also used if the $^{220}$Rn flux is being measured, to ensure adequate mixing of air in the chamber headspace.

Measurement procedure

Chambers are typically installed to a depth of ~ 5 cm, except on soils with a high air-filled porosity, on which they are inserted to a depth of ~ 10 cm or more, so as to reduce the risk of lateral diffusion beneath the side walls of the chamber. In order to minimise disturbance, a sharpened steel cutting ring or a knife is used to cut a circular groove into
the soil into which the chamber is pushed, ensuring a tight fit. The height of the headspace between the soil surface and the chamber lid, and the soil moisture content and soil temperature inside the chamber area, are then measured, whilst the AlphaGUARD is flushed with air from approximately mid-chamber height (in order to fill the ionisation chamber with air of ambient concentration). If the $^{220}$Rn flux is being measured the exhaust air is collected in the Tedlar bag. Once a large enough air sample has been collected, the pump is switched off and the chamber lid is securely fastened to the chamber rim with four plastic clips. The AlphaGUARD inlet and outlet tubes are then attached to the chamber using two 20 cm-long plastic tubes, which are inserted into the holes in the chamber lid. The time is then noted, the pump switched on, and the system left for 1-2 hours. A flow rate of 1 L min$^{-1}$ is generally used, except for when measuring fluxes from highly porous soils, on which the lowest flow rate (0.3 L min$^{-1}$) is used, so as to reduce the risk of inducing mass flow. At the end of the accumulation time the AlphaGUARD is flushed with ambient air after disconnection from the chamber, in order to minimise the build-up of $^{210}$Pb inside the ionisation chamber. The ambient air sample is then analysed on returning to the laboratory (by which time all of the $^{220}$Rn atoms will have decayed).

**Data quality control and corrections**

Data are downloaded from the AlphaGUARD using the AlphaEXPERT software and exported to Microsoft Excel. Data are quality-checked with reference to AlphaGUARD’s two quality assurance values (§3.3.1), and the rate of increase in radon activity ($A_{[Rn-222 + Rn-220]}$ after $^{220}$Rn has reached equilibrium, or $A_{Rn-222}$ if a delay volume was used) is checked for linearity. For consistency, six 10-min counts are used to calculate the $^{222}$Rn flux (Fig. 3.2), except for when longer counts/measurement times are necessary because of very small fluxes. Data with $r^2$ values less than a mean value based on 1000 random number simulations generated in an Excel spreadsheet, minus 3 standard deviations, are rejected. The ambient $^{222}$Rn activity ($A_{Rn-222,0}$), obtained from
analysis of an air sample in the laboratory (§3.3.3), is decay-corrected for the time between sampling and analysis, and $E_{220}$ is corrected for the proportion of $^{220}$Rn atoms which decay in transit between the chamber headspace and the AlphaGUARD’s active cell. $J_{Rn-222}$ and $J_{Rn-220}$ are then calculated as described in sections 3.2.2 and 3.2.3, respectively.

3.3.4 Measuring $^{222}$Rn fluxes by the grab-sampling method

The ‘grab-sampling’ method of measuring $^{222}$Rn fluxes, in which air samples are taken from the chamber headspace and later analysed in the laboratory using an automated analysis system, is the method used when more than one $^{222}$Rn flux measurement is required at one moment in time i.e. replicate measurements, and in studies of the local-scale spatial variability of $^{222}$Rn flux. Because of the very short half-life of $^{220}$Rn, it is not possible to measure the $^{220}$Rn flux by this method.

Equipment and measurement procedure

Measurements were carried out as described in §3.3.3, but instead of continuously monitoring the radon activity inside the chamber with the AlphaGUARD, an air sample was taken from the chamber headspace at the end of the accumulation period. Samples were collected in 1 L glass bottles, by circulating air between the bottle and chamber headspace at a flow rate of ~ 1 L min$^{-1}$ for ~ 5 minutes (Fig. 3.9). Each bottle has a rubber stopper seal with two tubing ports to enable circulation between the chamber and bottle in a closed loop. Prior to sampling, the sample bottles were left open, so that they contained air of ambient concentration. Ambient air samples were taken at the start and end of the flux measurements, the average value of which was used as the $A_{Rn-222,0}$ value in flux calculations (§3.2.2).
Automated analysis of $^{222}\text{Rn}$ in air samples

The automated analytical system essentially consists of the AlphaGUARD and AlphaPUMP; a 12-port rotary switching valve with a common inlet and outlet; a bottle of $^{222}\text{Rn}$-free air; and a PC, which operates the system. Figure 3.10 shows the flow-paths of the system when (a) loading and counting air samples, and (b) when flushing the AlphaGUARD with $^{222}\text{Rn}$-free air. When loading the air samples air is circulated in a closed loop between the AlphaGUARD and bottle by the AlphaPUMP (Fig. 3.10a). Air is drawn from the sample bottle via the common inlet and outlet of the rotary switching valve, which moves from one sample to the next by activation of a stepping motor. When flushing, the pressurised air forces the air contained in the AlphaGUARD and tubes out of the system, via a vent (Fig. 3.10b). The typical analysis time for one sample was 1 hour. This involved: 1) flushing the AlphaGUARD with $^{222}\text{Rn}$-free air for 10 min; 2) counting/measuring the radon activity for 10 min (in order to obtain the
instrument background; 3) circulating air between the bottle and AlphaGUARD for 10 min (loading the sample); and 4) counting/measuring the radon activity for 30 min.

Figure 3.10. Schematic diagram of the automated analytical system used for measuring the $^{222}$Rn activity of air samples: (a) the flow path (bold line) when loading and counting air samples, and (b) the flow path when flushing the system with $^{222}$Rn-free air.

**Data quality control and corrections**

Data were downloaded and quality checked and corrected as described in §3.3.3. To compare the continuous monitoring and grab-sampling methods, $^{222}$Rn fluxes were
measured simultaneously by the grab-sampling and continuous monitoring methods on a
number of occasions (Figure 3.11). Reasonable agreement was found between the two
methods (r = 0.73), but differences were as large as – 47% and + 60% for the grab-
sampling method relative to the continuous monitoring method. Overall, the grab-
sampling method was found to slightly underestimate fluxes compared to the continuous
monitoring method (for n = 44 the underestimate was 8% ± 26%). Experiments carried
out to further investigate this discrepancy showed that 222Rn activities measured in the
bottles were consistently lower than 222Rn activities measured inside the chamber
headspace, and that this was not due to the bottles leaking (data not shown). Inadequate
flushing of the bottle with chamber air (i.e. not flushing for long enough to bring the
bottle into equilibrium with the chamber air) is the most likely cause of this discrepancy.
For the purpose of this research it has been assumed that the fluxes measured by the

\[ r = 0.73 \]

\[ \text{Figure 3.11.} \ 222\text{Rn fluxes measured by the continuous monitoring and grab-sampling methods.} \]

For the continuous monitoring method the error bars are the standard error of the linear
regression, and for the grab-sampling method they are the combined errors of the chamber
headspace activity and the ambient air activity (each being the standard error of three 10 min
counts).
Chapter 3  

Methods

Continuous monitoring method are correct, and a correction factor of 8% has been applied to all reported grab-sampling fluxes (Chapter 6).

3.4 Sources of error associated with closed chamber measurements

3.4.1 Site disturbance
Trampling and compaction of the soil when installing chambers can significantly affect the rate of gas exchange. In order to minimise disturbance, a cutting ring or knife was used to install chambers, and permanent collars were installed where repeated measurements were made (Fig. 3.8a).

3.4.2 Altered diffusion gradient
Due to the progressive decrease in the diffusion gradient between the soil and the chamber headspace that occurs with time (due to the accumulation of gases in the chamber headspace - §2.5.2), the closed chamber method tends to underestimate fluxes (Denmead, 1979; Rayment, 2000). In very porous soils this error can be large, but in moist soils of medium to fine texture, an altered diffusion gradient is unlikely to be a significant problem as long as chamber deployment times are kept to a minimum, with the underestimation in flux being < 10% (Conen and Smith, 2000; Lehmann et al., 2004). Further, this effect can be minimised by maximising the chamber area and height (provided that there is sufficient analytical sensitivity to cope with the consequent dilution of the gas or gases in question). Lateral diffusion through the topsoil can also be a problem in soils of high porosity, however, the risk of this occurring can be reduced by inserting chambers to greater depths.

3.4.3 Exclusion of pressure changes
Closed chambers do not transmit changes in atmospheric pressure caused by turbulence unless they are vented for this purpose. Such variations in pressure can create horizontal pressure gradients of sufficient magnitude to induce mass flow in very porous soils;
however, this effect is considered to be small for the conditions found in most natural and agricultural soils (Conen and Smith, 1998). Some researchers strongly advocate the use of vented chambers (Hutchinson and Mosier, 1981; Livingston and Hutchinson, 1995), however, it has been shown that venting chambers can create larger errors than it is supposed to overcome, particularly in windy environments (Conen and Smith, 1998). For this reason, only closed chambers have been used in this research.

3.4.4 Temperature effects
Changes in the temperature of the chamber headspace air and underlying soil as a result of solar heating can be a significant problem for flux measurements, as it can dramatically affect the production rate of some gases and also affects trace gas concentrations on a per-volume basis (Matthias et al., 1980). This problem can be minimised by using chambers constructed from plastic and reflective materials, and keeping closure times to a minimum. As the production rate of radon is not directly affected by temperature, this problem is not a major concern for radon, unlike for biogenically-produced gases such as N₂O and CO₂. Changes in trace gas concentrations on a per-volume basis are unlikely to be a significant source of error over the range of temperature changes encountered in most environmental studies (Livingston and Hutchinson, 1995).

3.5 An intercomparison of three closed chamber $^{222}$Rn flux measurement techniques

3.5.1 Introduction
To test the validity of the ‘continuous monitoring’ method of measuring $^{222}$Rn fluxes used in this research, a comparison with two other closed chamber methods was carried out. The methods compared were the method described above in §3.3.3 (and used at the University of Edinburgh), and those used at the University of Nagoya Department of Nuclear Engineering, Japan, and the National Institute of Radiological Sciences (NIRS),
Japan. All three methods use closed (or static) accumulators, but differ in terms of the method of $^{222}$Rn detection employed and chamber design. Two separate intercomparison studies were carried out in Japan in 2003: the first at Nagoya University, Higashiyama campus, between 31st March and 4th April, and the second at NIRS, Chiba, on 10th April.

3.5.2 $^{222}$Rn flux measurement methods

University of Edinburgh method
This method used was that described in §3.3.3, using the 40 cm diameter chamber (§3.3.2).

University of Nagoya method
The chamber is a cylindrical metal container which is open at one end and has dimensions of 28 cm diameter and 10 cm height (Figure 3.12). The chamber has two sampling valves and is typically inserted into the soil to a depth of ~ 1 cm. The accumulation time is 15 min, after which two air samples are drawn from the chamber

Figure 3.12. The chamber used to measure $^{222}$Rn flux by researchers at the University of Nagoya Department of Nuclear Engineering. The chamber has a diameter of 28 cm, and is 10 cm high.
headspace into evacuated 5 L polyvinyl fluoride bags, using a diaphragm pump (Iida et al., 1991). At the beginning of the measurement two ambient air samples are taken, which are analysed for $^{222}$Rn in the laboratory using the $^{222}$Rn monitor developed by Iida et al., (1991), which employs electrostatic collection of $^{218}$Po ions and scintillation counting.

**National Institute of Radiological Sciences method**

The NIRS method uses the instrument developed by M. Shimo and co-workers (Saegusa et al., 1996). This consists of a pyramid-shaped chamber with a zinc-sulphide scintillator and photomultiplier tube mounted on top (Figure. 3.13), and an 11 cm-high rectangular 'skirt', from which the upper part of the instrument can be detached. The chamber has a base area of 40 cm x 30 cm, and a total volume of ~ 0.012 m$^3$. It is typically inserted into the ground to a depth of ~ 1 cm. The total radon count ($A_{[Rn-222+Rn-220]}$) is recorded at 1 min intervals and is displayed on a hand-held computer.

![Figure 3.13. Schematic diagram of the radon flux meter used by researchers at NIRS (from Saegusa et al., 1996).](image)
The counting efficiency of the instrument is ~ 20%. For a 30-minute accumulation time and a detection limit equal to three times the standard deviation of the background count, the instrument has a lower limit of detection of 25 Bq m\(^{-2}\) h\(^{-1}\). The \(^{222}\)Rn count is determined by subtracting the counts due to instrument background and the counts due to \(^{220}\)Rn from the total count rate.

### 3.5.3 Field sites and experimental design

#### University of Nagoya study

Measurements were made at two separate bare-soil sites within a few hundred metres of the Department of Nuclear Engineering premises. The first site was on a dry and stony soil approximately 5 m from the Department of Nuclear Engineering building. The second was on the edge of a ploughed field (Figure 3.14). The first site was expected to have lower \(^{222}\)Rn emissions than the second because the soil was very dry and stony at this site, and thus it would be likely that the amount of radon escaping to pore space (emanating fraction - §2.2.1) would be much less. For each set of measurements, \(^{222}\)Rn

*Figure 3.14. The Edinburgh University (top) and Nagoya University (bottom) chambers on the edge of a ploughed field at the Higashiyama campus, Nagoya University.*
fluxes were measured simultaneously by the Edinburgh and Nagoya systems, and then the chambers were exchanged so that each chamber covered the same patch of soil the other chamber had previously occupied. Prior to the second measurement the soil was left uncovered (or the chamber lid removed) for at least the same length of time as it had been in place, so as to allow soil gas concentrations to readjust (§3.4.2). Also, at the end of the accumulation time, air samples were taken from the Edinburgh chamber by the Nagoya method, and were analysed using the electrostatic monitor (Iida et al., 1991). Various environmental parameters (e.g. atmospheric pressure, air and soil temperature, soil moisture) were monitored throughout the duration of the flux measurements.

National Institute of Radiological Sciences study
Measurements were made on a patch of bare soil site ~5m from a building on the NIRS campus, Chiba. The measurement procedure was the same as at Nagoya, with chambers removed or left open between measurements; however, as there were three sets of flux measurement instrumentation, the measurements were carried out in rotation. For the Nagoya method, $^{222}\text{Rn}$ was determined by zinc-sulphide scintillation counting using an AB-5 Lucas chamber, rather than the electrostatic monitor used at Nagoya.

3.5.4 Results

University of Nagoya study
At the dry and stony site no significant flux of $^{222}\text{Rn}$ was detected by either method (data not shown). Significant emissions of $^{222}\text{Rn}$ have previously been measured at this location (Iida et al., 1991), hence, it seems likely that on this occasion the amount of $^{222}\text{Rn}$ escaping from the soil (the emanating fraction), and thus the $^{222}\text{Rn}$ flux, was limited by the very low moisture content of the soil (Strong and Levins, 1982; Stranden et al., 1984), which was $<0.1\text{ m}^3\text{ m}^{-2}$. 
$^{222}$Rn fluxes measured at two adjacent spots at the ploughed field site (Fig. 3.14) are shown in Figure 3.15, and are summarised in Table 3.1. 'Edinburgh (E)' fluxes are fluxes measured using the Edinburgh chamber with analysis of air samples by the Nagoya University electrostatic monitor. The measurements made at this site were carried out over two days, during which the weather conditions were relatively constant. Atmospheric pressure gradually decreased over the course of measurements (data not shown), but this was by < 1% from start to finish of the flux measurements. On the second day (4th April) there was a few light rain showers, but these mostly occurred

![Figure 3.15](image-url)

Figure 3.15. $^{222}$Rn fluxes measured at two adjacent spots (A and B) on the edge of a ploughed field at Nagoya University Higashiyama campus, using three different methods (Edinburgh, Edinburgh (E), and Nagoya). Edinburgh (E) fluxes are fluxes determined from analysis of an air sample from the Edinburgh chamber headspace by the Nagoya method (electrostatic collection of $^{210}$Po and scintillation counting). Error bars for the fluxes measured by the Edinburgh method are the standard error of the linear regression, and those for the fluxes measured by the Nagoya and Edinburgh (E) methods are combined errors of the chamber headspace $^{222}$Rn activity and the ambient air $^{222}$Rn activity.
Table 3.1. Mean $^{222}$Rn fluxes (Bq m$^{-2}$ h$^{-1}$) measured at two adjacent spots at Nagoya University Higashiyama campus, using three different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>No. of obs.</th>
<th>Location A</th>
<th>Location B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Std. dev.</td>
</tr>
<tr>
<td>Edinburgh</td>
<td>3</td>
<td>55</td>
<td>23</td>
</tr>
<tr>
<td>Nagoya</td>
<td>3</td>
<td>47</td>
<td>30</td>
</tr>
<tr>
<td>Edinburgh (E)$^1$</td>
<td>3</td>
<td>42</td>
<td>3</td>
</tr>
<tr>
<td>All measurements</td>
<td>9</td>
<td>48</td>
<td>20</td>
</tr>
</tbody>
</table>

$^1$The Edinburgh chamber and $^{222}$Rn analysis using the Nagoya method (electrostatic collection of $^{218}$Po ions and scintillation counting).

When the chambers were in place and sealed. Soil moisture did not significantly change over the duration of measurements (mean soil moisture contents recorded at the start of each set of measurements were: 34%, 28% and 28% at spot A, and 33%, 30% and 27% at spot B). Thus, temporal variations in environmental conditions can largely be discounted as a factor contributing to the observed variability in $^{222}$Rn fluxes. Given the good agreement between the mean fluxes recorded at locations A and B for each of the methods (Table 3.1), and that there was no significant difference in soil moisture levels between these two spots of measurement, it can also be considered that spatial inhomogeneity between the two spots of measurement would not have significantly contributed to the observed variability either. Hence, it is reasonable to consider that the observed variability in measured $^{222}$Rn fluxes is due to the differences between the methods, and the fluxes recorded at locations A and B can be pooled for further analysis (Table 3.2). From Table 3.2, it can be seen that Edinburgh (E) method was most precise (CV = 15%), and the Edinburgh and Nagoya methods gave more variable results, with coefficients of variation of ~ 40%. The coefficient of variation for all measurements – indicating the collective precision of all methods – was 37%.
Table 3.2. Mean $^{222}$Rn fluxes (Bq m$^{-2}$ h$^{-1}$) and coefficients of variation (C.V.) for the pooled Nagoya University measurements (fluxes measured at locations A and B).

<table>
<thead>
<tr>
<th>Method</th>
<th>No. of obs.</th>
<th>Mean</th>
<th>Std. dev.</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edinburgh</td>
<td>6</td>
<td>52</td>
<td>22</td>
<td>42</td>
</tr>
<tr>
<td>Nagoya</td>
<td>6</td>
<td>49</td>
<td>19</td>
<td>39</td>
</tr>
<tr>
<td>Edinburgh (E)$^1$</td>
<td>6</td>
<td>39</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>All measurements</td>
<td>18</td>
<td>46</td>
<td>17</td>
<td>37</td>
</tr>
</tbody>
</table>

$^1$The Edinburgh chamber and $^{222}$Rn analysis using the Nagoya method (electrostatic collection of $^{214}$Po ions and scintillation counting).

National Institute of Radiological Sciences study

$^{222}$Rn fluxes measured at NIRS are shown in Figure 3.16, and are summarised in Table 3.3. ‘Nagoya (Zn-S)’ fluxes are those measured using the Nagoya chamber and $^{222}$Rn detection using a Lucas chamber, rather than the electrostatic deposition method used at Nagoya University. During the course of measurements, atmospheric pressure remained virtually constant (data not shown), and conditions were dry throughout the day. Mean soil moisture contents at the three spots of measurement A, B and C were: 35%, 33% and 32% respectively. Thus, as in the case of the Nagoya data set, the observed variability in $^{222}$Rn fluxes can be considered to be largely due to the differences between the methods, and the data can be pooled for analysis (Table 3.4). From Table 3.4 it can be seen that the Nagoya (Zn-S) method was the most precise (C.V = 17%). The Edinburgh and NIRS methods showed similar levels of precision, but were more variable than the Nagoya (Zn-S) method, with coefficients of variation of 48% and 42%, respectively. The coefficient of variation for all measurements (indicating the collective precision of all methods) was 36%.
Figure 3.16. $^{222}$Rn fluxes measured at three adjacent spots (A, B and C) on a patch of bare soil at NIRS, Chiba, using three different methods (Edinburgh, Nagoya (Zn-S) and NIRS). Nagoya (Zn-S) fluxes are fluxes determined using the Nagoya chamber and with $^{222}$Rn analysis using a Lucas chamber (instead of the electrostatic deposition monitor). Error bars for the fluxes measured by the Edinburgh and NIRS methods are the standard error of the linear regression, and the error bars for fluxes measured by the Nagoya (Zn-S) method are combined errors of the chamber headspace $^{222}$Rn activity and the ambient air $^{222}$Rn activity.

Table 3.3. Mean $^{222}$Rn fluxes (Bq m$^{-2}$ h$^{-1}$) measured at three adjacent locations at NIRS, using three different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>No. of obs.</th>
<th>Location A</th>
<th>Location B</th>
<th>Location C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Location A</td>
<td>Location B</td>
<td>Location C</td>
</tr>
<tr>
<td>Edinburgh</td>
<td>1</td>
<td>35</td>
<td>16</td>
<td>49</td>
</tr>
<tr>
<td>NIRS</td>
<td>1</td>
<td>44</td>
<td>46</td>
<td>19</td>
</tr>
<tr>
<td>Nagoya (Zn-S)</td>
<td>3</td>
<td>32</td>
<td>32</td>
<td>24</td>
</tr>
<tr>
<td>All measurements</td>
<td>3</td>
<td>37, 6</td>
<td>31, 15</td>
<td>31, 16</td>
</tr>
</tbody>
</table>

*The Nagoya chamber and $^{222}$Rn analysis using a Lucas chamber (instead of the electrostatic deposition monitor used at Nagoya).*
Table 3.4. Mean $^{222}$Rn fluxes (Bq m$^{-2}$ h$^{-1}$) and coefficients of variation (C.V.) for the pooled NIRS measurements (fluxes measured at locations A, B and C).

<table>
<thead>
<tr>
<th>Method</th>
<th>No. of obs</th>
<th>Mean</th>
<th>Std. dev</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edinburgh</td>
<td>3</td>
<td>33</td>
<td>16</td>
<td>48</td>
</tr>
<tr>
<td>NIRS</td>
<td>3</td>
<td>36</td>
<td>15</td>
<td>42</td>
</tr>
<tr>
<td>Nagoya (Zn-S)</td>
<td>3</td>
<td>29</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td>All measurements</td>
<td>9</td>
<td>33</td>
<td>12</td>
<td>36</td>
</tr>
</tbody>
</table>

1The Nagoya chamber and $^{222}$Rn analysis using a Lucas chamber (instead of the electrostatic deposition monitor used at Nagoya).

3.5.5 Discussion and conclusions

Mean $^{222}$Rn fluxes were found to be in good agreement for all methods, in both studies (Tables 3.2 and 3.4), and individual measurements generally overlapped within the range of error (Figs. 3.15 and 3.16). No systematic differences were observed between the different methods, but the Edinburgh (E) and Nagoya (Zn-S) methods were the most precise, with coefficients of variation of 15% and 17% respectively, compared to 42% and 48% for the Edinburgh method (for the Nagoya and NIRS studies, respectively); 39% for the Nagoya method (with $^{222}$Rn detection by electrostatic monitor); and 42% for the NIRS method (Tables 3.2 and 3.4). Coefficients of variation for the pooled data (i.e. a measure of the collective precision of all methods) were 37% for the Nagoya study and 36% for the NIRS study. This level of agreement is similar to that found for field measurements carried out during international intercomparison exercises held in the US (CV = 34%) (Hutter and Knutson, 1998) and in the Czech Republic (CV = 43%) (Neznal and Neznal, 2002). Thus, it can be considered that, with regard to current $^{222}$Rn flux methodology standards, the different techniques agree reasonably within the range of errors, and that the method used in this research is satisfactory.
Chapter 4

Temporal studies of $^{222}$Rn and $^{220}$Rn flux

4.1 Introduction

A large number of studies have investigated the temporal variability in $^{222}$Rn emissions on the day-to-day time-scale (e.g. Schery, et al., 1984; Dueñas and Fernandez, 1987; Koarashi et al., 2000), but time-series data on the seasonal or diurnal time-scales are limited, and for $^{220}$Rn there are very few data published in the literature, in general (§2.5.2). Water table depth, a factor which is known to be important for controlling fluxes of other gases emitted or taken-up by the soil, such as CO$_2$ and CH$_4$ and N$_2$O (Chimmer and Cooper, 2003; MacDonald et al., 1998), does not appear to have been included in any studies of $^{222}$Rn flux (§2.3.1). Studies reporting the effects of freezing of the soil and/or snow cover on radon emissions are also scarce, and some of these suggest that assumptions of very low or zero emissions from frozen and snow-covered soils need to be re-assessed (e.g. Morizumi et al., 2004; §2.3.1).

In this chapter, the results of studies carried out to investigate the temporal variability in $^{222}$Rn and $^{220}$Rn emissions on the short (< 1 day to 1 week) and seasonal time-scales are presented and discussed. In particular, these studies have been concerned with the effects of rainfall, water table depth, and freezing of the soil surface, and the degree of variability in emissions on the diurnal, day to day and seasonal time-scales. Two short-term studies were carried out: one in summer and one in winter ($^{222}$Rn flux only), and one study over a full season ($^{222}$Rn and $^{220}$Rn fluxes). The importance of water table
depth as a factor controlling $^{222}$Rn emissions was also investigated in the laboratory, using a soil monolith.

4.2 Methods

4.2.1 Field site

Measurements were made at two locations approximately 6 m apart on a plot of bare soil in the University of Edinburgh botany garden, Kings Buildings, Edinburgh (55°10'N, 2°03'W). The short-term studies were carried out at one location, and the seasonal time-scale study at the other. The soil at this site is a medium-textured sandy loam, and the mean bulk density was 1.1 Mg m$^{-3}$. The bedrock is Old Red Sandstone of the upper Devonian period, and, according to geological maps, the area is overlain with boulder clay. However, the particle size analysis (mean particle size fractions of 6% clay, 33% silt and 61% sand) suggests that this is not the case for this site, where the soil and any unconsolidated deposits are likely to have been modified considerably from their natural condition and composition, as a result of construction work carried out during the 1930s. Also, the application of rock phosphate-containing fertilizers could possibly have enhanced the $^{226}$Ra and $^{224}$Ra content of the soil. Mean equivalent $^{226}$Ra and $^{224}$Ra activities of the top 10 cm of the soil at this site were 33 Bq kg$^{-1}$ and 22 Bq kg$^{-1}$, respectively. This is somewhat higher than would be expected from an untreated soil developed on sandstone (Keller and Schütz, 1988; Chapter 5 – Table 5.4; §4.3.1 below).

4.2.2 Diurnal studies

The summer diurnal study was carried out between 11th and 23rd July 2001, during a period of weather which was characterised by heavy rain showers and sunshine, and the winter study was carried out between 21st December 2001 and 10th January 2002, during a spell of frosty weather. The $^{222}$Rn flux was measured by the continuous monitoring method (§3.3.3), using an automatic flux chamber of the same design used by Smith and Dobbie (2001) (Figs. 4.1 and 3.8c). The automatic flux chamber is 30 cm
high with a 2 cm wide horizontal flange at the top. A rubber gasket containing a magnetic strip of the type used to seal doors of domestic fridges is cemented to the underside. The lid is pivoted by two pairs of arms on opposite sides of the chamber. Closure and re-opening is achieved by an electrically powered (24 V DC) actuator, which is attached to a steel extension frame bolted to the chamber. A more detailed description of this chamber can be found in Smith and Dobbie (2001).

![Diagram of the automatic static flux chamber](image)

**Figure 4.1.** The automatic static flux chamber (from Smith and Dobbie, 2001).

The chamber was installed to a depth of 3 cm, and the AlphaGUARD was connected to the autochamber with an approximately 10 m length of hard plastic tubing. The instrument and pump were stored in a nearby hut with a mains electricity supply. Six flux measurements were made per day, with the chamber closed between 0340-0500h, 0740-0900h, 1140-1300h, 1540-1700h, 1940-2100h, and 2340-0100h. Thus, the chamber was closed for 1 hour 20 min and kept open for 2 hours 40 min between each measurement. This allowed ample time for flushing of the AlphaGUARD ionisation chamber between measurements, and for soil gas concentrations to readjust after the closure period (§3.4.2). Atmospheric pressure, air temperature and humidity inside the chamber were continuously recorded by the AlphaGUARD, and the soil moisture content and water table depth were recorded at intervals throughout the experiment. Soil
moisture content (volumetric) was measured using a ThetaProbe (Delta-T Devices Ltd, Cambridge, UK), and water table depth was measured by inserting a stick into a dip-well. During the winter study, the soil temperature at 1 cm depth was monitored continuously using a copper-constantan thermocouple and a Campbell Scientific CR500 data logger. Precipitation was recorded using a tipping-bucket rain gauge. The soil bulk density was determined using 6 cm diameter by 4 cm length bulk density collars (5 replicates).

4.2.3 Seasonal study

$^{222}$Rn and $^{220}$Rn fluxes were measured approximately twice per week between October 2000 and December 2001, using the continuous monitoring method (§3.3.3). A plastic collar for the manually operated 40 cm chamber (Fig 3.8, Chapter 3) was permanently installed at this location (to a depth of 4 cm), so as to prevent repeated disruption of the soil. During measurements, a water seal was maintained between the collar and chamber by means of an inverted glass bottle filled with water, and supported by a clamp (Fig. 3.8a). Measurements were carried out at approximately the same time of day (between 1200h and 1400h). During each flux measurement the atmospheric pressure, air temperature and humidity inside the chamber were continuously monitored by the AlphaGUARD, and, at the start of each measurement the soil moisture and water table depth were recorded as described above (§4.2.2). At the beginning and end of each flux measurement the soil temperature at the surface and at 10 cm depth was also recorded, using a hand-held digital thermometer (Quartz Instruments Digi-thermo). Precipitation was recorded using a tipping-bucket rain gauge.

4.2.4 Soil monolith study

A soil core was obtained on 26th July 2002, from the location where the seasonal study measurements were carried out. The core was obtained by inserting a 52 cm length of plastic tubing (25 cm diameter) into the ground to ensleeve a soil column, which was
then undercut and removed as an undisturbed monolith. This was a miniaturized version of the collection procedure of Thomson et al. (1997). In the laboratory, the core was placed in a 50 cm-deep bucket, and the water table was manipulated by adding water to the bucket.

### 4.3 Results

#### 4.3.1 Diurnal studies

**Summer study (11th-23rd July 2001)**

Summary statistics for all variables recorded are given in Table 4.1, and $^{222}$Rn fluxes, atmospheric pressure, water table depth, and the amount of rainfall which fell when the chamber was open in-between each flux measurement are shown in Figure 4.2. All variables were approximately normally distributed, except for rainfall, which was log-normally distributed. The mean $^{222}$Rn flux was 29.3 Bq m$^{-2}$ h$^{-1}$. This is much higher

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs</th>
<th>Mean</th>
<th>Median</th>
<th>Std. dev.</th>
<th>Min.</th>
<th>Max.</th>
<th>Skewness</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>71</td>
<td>29.3</td>
<td>30.0</td>
<td>9.8</td>
<td>-4.1</td>
<td>50.3</td>
<td>-0.92</td>
<td>34</td>
</tr>
<tr>
<td>Soil moisture (m$^3$ m$^{-2}$)</td>
<td>7</td>
<td>0.33</td>
<td>0.34</td>
<td>0.03</td>
<td>0.28</td>
<td>0.37</td>
<td>-1.07</td>
<td>9</td>
</tr>
<tr>
<td>Water table depth (m)</td>
<td>18</td>
<td>0.57</td>
<td>0.57</td>
<td>0.30</td>
<td>0.54</td>
<td>0.62</td>
<td>0.40</td>
<td>53</td>
</tr>
<tr>
<td>Rainfall (mm)</td>
<td>71</td>
<td>0.4</td>
<td>0.0</td>
<td>0.1</td>
<td>8.0</td>
<td>0</td>
<td>4.34$^a$</td>
<td>278</td>
</tr>
<tr>
<td>Atmospheric pressure (hPa)</td>
<td>71</td>
<td>1001</td>
<td>1001</td>
<td>5</td>
<td>988</td>
<td>1009</td>
<td>-0.48</td>
<td>0</td>
</tr>
<tr>
<td>Change in atmospheric pressure (%)</td>
<td>70</td>
<td>0.03</td>
<td>0.00</td>
<td>0.10</td>
<td>-0.20</td>
<td>0.30</td>
<td>-0.20</td>
<td>363</td>
</tr>
<tr>
<td>Air temperature inside chamber (°C)</td>
<td>71</td>
<td>17.5</td>
<td>17.0</td>
<td>3.0</td>
<td>12</td>
<td>24</td>
<td>0.50</td>
<td>17</td>
</tr>
<tr>
<td>Soil surface temperature (°C)</td>
<td>15</td>
<td>18.3</td>
<td>18.3</td>
<td>4.6</td>
<td>15.5</td>
<td>30.7</td>
<td>1.05</td>
<td>23</td>
</tr>
<tr>
<td>Soil temperature at 10 cm (°C)</td>
<td>15</td>
<td>16.1</td>
<td>16.0</td>
<td>1.6</td>
<td>14.3</td>
<td>19.7</td>
<td>0.80</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$Change in atmospheric pressure is the change relative to the mean value recorded during the previous flux measurement.

$^b$Skewness after log-e transformation was -0.46
Figure 4.2. Measurements made at a bare soil site in the University of Edinburgh botany garden between 11th and 23rd July 2001: (a) $^{222}$Rn fluxes and atmospheric pressure, and (b) rainfall and water table depth. $^{222}$Rn flux error bars are the standard error of the linear regression, and dashed lines are $\pm 1$ standard deviation of the mean. The rainfall value corresponding to each flux measurement is the amount which fell in the period when the chamber was open prior to that measurement.
than mean values which have been reported for soils developed on sandstone by others (e.g. Keller and Schütz, 1988; Ielsch et al., 2001), and suggests that the $^{226}\text{Ra}$ and $^{224}\text{Ra}$ content of the soil at this site could possibly have been enhanced as a result of the application of rock phosphate-containing fertilisers. The coefficient of variation for $^{222}\text{Rn}$ flux was 34%. A multiple correlation analysis found that the $^{222}\text{Rn}$ flux was weakly correlated with atmospheric pressure ($r = 0.38$), but not with any other variable.

The first few days of the study (10th to 14th July) were characterised by frequent rain showers, particularly on 12th July (Fig. 4.2). From 15th to 18th July there was a spell of dry weather, after which the showery weather returned. Over the period of measurements the water table dropped by 10 cm, from 0.54 m on the 11th to 0.64 m on the 23rd. Mean soil moisture contents recorded on the 12th, 13th and 15th were 0.32, 0.36 and 0.33 m$^3$ m$^{-3}$, respectively. The $^{222}\text{Rn}$ flux varied between 20 and 40 Bq m$^{-2}$ h$^{-1}$ for much of the time. On 18/19th July, between 1230h and 0030h, there was a short-lived peak in $^{222}\text{Rn}$ flux which coincided with the end of the dry spell of weather, and thus most likely the lowest soil moistures (soil moisture was not recorded on this day). On the evening of the 20th, heavy rainfall led to a total suppression of the $^{222}\text{Rn}$ flux for ~6-8 hours, after which the flux increased to about a third of its value prior to rainfall. By 1630h the following day the flux had returned to within 1$\sigma$ of the mean.

Figure 4.3 shows the mean $^{222}\text{Rn}$ flux, air temperature (chamber headspace), and atmospheric pressure for each measurement time for the days on which there was no rainfall (15th, 16th, 17th and 22nd), and Table 4.2 shows mean $^{222}\text{Rn}$ fluxes, air temperatures, and atmospheric pressures for the data pooled according to whether the measurements were made before midday (0030h, 0430h and 0830h) or after midday (1230h, 1630h and 2030h). A trend of larger fluxes during the afternoon and early evening (between 1200h and 2000h) compared to those recorded during the night and morning (between 0000h and 0800h), and higher temperatures and slightly greater
Figure 4.3. Mean $^{222}$Rn fluxes, air temperatures (chamber headspace) and atmospheric pressures for each measurement time on the days unaffected by rainfall ($n=4$). $^{222}$Rn flux error bars are 1 standard deviation.

Table 4.2. Mean $^{222}$Rn fluxes, air temperatures and atmospheric pressures for the days unaffected by rainfall, pooled according to measurement time before midday or after midday.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Before midday</th>
<th>After midday</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of obs.</td>
<td>Mean</td>
</tr>
<tr>
<td>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>12</td>
<td>28.8</td>
</tr>
<tr>
<td>Air temperature inside chamber (°C)</td>
<td>12</td>
<td>15.8</td>
</tr>
<tr>
<td>Atmospheric pressure (hPa)</td>
<td>12</td>
<td>1004</td>
</tr>
</tbody>
</table>
atmospheric pressures in the afternoon is apparent in the data (Fig. 4.3; Table 4.2). A one-way analysis of variance (ANOVA) confirmed that there was a significant difference between the before midday and after midday mean $^{222}$Rn fluxes (25% higher; $p < 0.05$) and mean air temperatures ($5^\circ C$ higher; $p < 0.05$), but not between mean atmospheric pressures.

**Winter study (21st December – 10th January)**

$^{222}$Rn fluxes, the soil temperature at 1 cm depth, and atmospheric pressure recorded during 21st December – 10th January are shown in Figure 4.4, and $^{222}$Rn fluxes and soil temperatures for the period 3rd – 10th January only are shown in Figure 4.5. Summary statistics are given in Table 4.3. The mean $^{222}$Rn flux was 27.2 Bq m$^{-2}$ h$^{-1}$, and the coefficient of variation 25%. A multiple correlation analysis found the $^{222}$Rn flux to be weakly correlated with air pressure ($r = 0.34$) and soil temperature ($r = -0.26$), but not with any other variable. Due to malfunctions with the autochamber no data were recorded between 22nd and 27th of December, or 29th December and 3rd January. For the first period of measurements (21st – 22nd Dec) the soil surface was mostly frozen, to

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs</th>
<th>Mean</th>
<th>Median</th>
<th>Std. dev.</th>
<th>Min</th>
<th>Max</th>
<th>Skewness</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>56</td>
<td>27.2</td>
<td>27.4</td>
<td>6.7</td>
<td>14.2</td>
<td>39.7</td>
<td>-0.14</td>
<td>25</td>
</tr>
<tr>
<td>Chamber air temperature (°C)</td>
<td>120</td>
<td>4.5</td>
<td>4.2</td>
<td>3.3</td>
<td>-3.6</td>
<td>10.9</td>
<td>0.10</td>
<td>72</td>
</tr>
<tr>
<td>Soil temperature at 1 cm (°C)</td>
<td>120</td>
<td>-0.2</td>
<td>3.5</td>
<td>-8.9</td>
<td>8.4</td>
<td>0.30</td>
<td>0.30</td>
<td>897</td>
</tr>
<tr>
<td>Atmospheric pressure (hPa)</td>
<td>119</td>
<td>1009</td>
<td>1016</td>
<td>14</td>
<td>974</td>
<td>1025</td>
<td>-0.59</td>
<td>1</td>
</tr>
<tr>
<td>Change in atmospheric pressure (%)$^a$</td>
<td>119</td>
<td>0.02</td>
<td>0.00</td>
<td>0.23</td>
<td>-0.70</td>
<td>0.82</td>
<td>0.13</td>
<td>1513</td>
</tr>
</tbody>
</table>

$^a$Change in atmospheric pressure is the change relative to the mean value recorded during the previous flux measurement.
Figure 4.4. $^{222}$Rn fluxes, soil temperature at 1 cm depth, and atmospheric pressure recorded at a bare soil site in the Edinburgh University botany garden between 21st December 2001 and 10th January 2002. $^{222}$Rn flux error bars are the standard error of the linear regression, and the short dashed lines are ±1 standard deviation of the mean. Missing flux data are due to malfunctions of the autochamber.
Figure 4.5. $^{222}$Rn fluxes and the soil temperature at 1 cm depth measured at a bare soil site in the Edinburgh University botany garden between 3rd and 10th January 2002. $^{222}$Rn flux error bars are the standard error of the regression line, and the continuous heavy line shows the moving average of the mean of every three measurements.
a maximum depth of ~ 4 cm, but from the 5th onwards it thawed, at first slowly, and then more quickly from ~ 0000h on the 7th. By 1600h on 8th January the soil had completely thawed and remained unfrozen until the end of the study. Throughout the duration of the experiment there was no precipitation, and thus no snow cover, and between 3rd and 10th January the atmospheric pressure remained almost constant (Fig. 4.4). Water table depth was virtually unchanged over the whole period, from 49 cm on the 3rd, to 50 cm on the 10th (data not shown). The mean soil moisture content recorded on the 10th was $0.34 \pm 0.04$ m$^3$ m$^{-3}$. The only notable trend in the data was slightly lower than average emissions towards the end of the thawing period (Fig. 4.5).

Mean $^{222}$Rn fluxes and soil temperatures for six sub-periods, divided according to whether the soil was frozen, unfrozen, or thawing, are shown in Table 4.4. A one-way ANOVA test confirmed there was no significant difference between mean $^{222}$Rn fluxes for the different periods ($p = 0.11$). For soil temperature the difference between means was found to be significant ($p < 0.001$).

Table 4.4. Mean $^{222}$Rn fluxes and soil temperatures for six time periods when the soil surface was unfrozen, frozen, or thawing.

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Soil Condition</th>
<th>No. of obs</th>
<th>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</th>
<th>Soil temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>Std. dev.</td>
</tr>
<tr>
<td>21st - 22nd Dec</td>
<td>Mostly frozen</td>
<td>4</td>
<td>24.3</td>
<td>5.2</td>
</tr>
<tr>
<td>27th - 29th Dec</td>
<td>Mostly unfrozen</td>
<td>10</td>
<td>23.6</td>
<td>7.4</td>
</tr>
<tr>
<td>3rd - 5th Jan</td>
<td>Frozen</td>
<td>11</td>
<td>29.2</td>
<td>5.5</td>
</tr>
<tr>
<td>5th - 6th Jan</td>
<td>Thawing slowly</td>
<td>10</td>
<td>30.6</td>
<td>5.2</td>
</tr>
<tr>
<td>7th - 8th Jan</td>
<td>Thawing quickly</td>
<td>10</td>
<td>24.8</td>
<td>5.8</td>
</tr>
<tr>
<td>8th - 10th Jan</td>
<td>Unfrozen</td>
<td>11</td>
<td>28.7</td>
<td>8.0</td>
</tr>
<tr>
<td>All data</td>
<td></td>
<td>56</td>
<td>27.2</td>
<td>6.7</td>
</tr>
</tbody>
</table>
4.3.2 Seasonal study

Summary statistics for all variables recorded are shown in Table 4.5, and $^{222}\text{Rn}$ and $^{220}\text{Rn}$ fluxes, water table depth, soil moisture, and rainfall measured between October 2001 and December 2002 are shown in Figure 4.6. All variables were approximately normally distributed, except for $^{220}\text{Rn}$ flux and rainfall. Summer and winter averages for

Table 4.5. Seasonal data summary statistics.

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs</th>
<th>Mean (Bq m$^{-2}$ h$^{-1}$)</th>
<th>Std. dev</th>
<th>Median</th>
<th>Quart. dev</th>
<th>Min.</th>
<th>Max</th>
<th>Skewness</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}\text{Rn}$ flux</td>
<td>92</td>
<td>42.4</td>
<td>16.6</td>
<td>39.0</td>
<td>9.6</td>
<td>11.3</td>
<td>92.4</td>
<td>0.78</td>
<td>39</td>
</tr>
<tr>
<td>$^{220}\text{Rn}$ flux</td>
<td>91</td>
<td>1136</td>
<td>1012</td>
<td>821</td>
<td>593</td>
<td>-23</td>
<td>5311</td>
<td>1.48*</td>
<td>89</td>
</tr>
<tr>
<td>Ambient $^{222}\text{Rn}$ concentration at 20 cm (Bq m$^{-3}$)</td>
<td>91</td>
<td>10.0</td>
<td>3.8</td>
<td>9.8</td>
<td>2.5</td>
<td>3.2</td>
<td>24.2</td>
<td>0.84</td>
<td>38</td>
</tr>
<tr>
<td>Soil moisture (m$^3$ m$^{-3}$)</td>
<td>68</td>
<td>0.35</td>
<td>0.05</td>
<td>0.36</td>
<td>0.03</td>
<td>0.21</td>
<td>0.44</td>
<td>-0.58</td>
<td>14</td>
</tr>
<tr>
<td>Water table depth (m)</td>
<td>72</td>
<td>0.51</td>
<td>0.15</td>
<td>0.48</td>
<td>0.11</td>
<td>0.20</td>
<td>0.74</td>
<td>0.25</td>
<td>30</td>
</tr>
<tr>
<td>Rainfall (mm)</td>
<td>218</td>
<td>3.2</td>
<td>4.8</td>
<td>1.4</td>
<td>2.0</td>
<td>0.0</td>
<td>30.0</td>
<td>2.60b</td>
<td>149</td>
</tr>
<tr>
<td>Atmospheric pressure (hPa)</td>
<td>91</td>
<td>1001</td>
<td>13.5</td>
<td>1001</td>
<td>8.5</td>
<td>975</td>
<td>1035</td>
<td>0.16</td>
<td>1</td>
</tr>
<tr>
<td>Chamber air temperature (°C)</td>
<td>91</td>
<td>16</td>
<td>6.9</td>
<td>15</td>
<td>4.5</td>
<td>5</td>
<td>36</td>
<td>0.71</td>
<td>42</td>
</tr>
<tr>
<td>Soil surface temperature (°C)</td>
<td>76</td>
<td>9.8</td>
<td>7.0</td>
<td>8.6</td>
<td>4.8</td>
<td>-0.2</td>
<td>26.4</td>
<td>0.55</td>
<td>72</td>
</tr>
<tr>
<td>Soil temperature at 10cm (°C)</td>
<td>79</td>
<td>8.7</td>
<td>6.0</td>
<td>7.7</td>
<td>4.9</td>
<td>0.1</td>
<td>20.6</td>
<td>0.35</td>
<td>69</td>
</tr>
</tbody>
</table>

*Skewness of log-e transformed data was -0.77
bSkewness of log-e transformed data was -0.10
Figure 4.6. Measurements made at a bare soil site in the University of Edinburgh botany garden between Oct 2001-Dec 2002: (a) $^{222}$Rn flux, (b) water table depth, (c) soil moisture (circles) and rainfall (bars), and (d) $^{220}$Rn flux. In (a) and (d) the continuous lines show the moving averages for monthly means ($^{222}$Rn) and medians ($^{220}$Rn), respectively. Dashed lines are the mean ($^{222}$Rn) and median ($^{220}$Rn) fluxes.
radon fluxes, soil moisture, and water table depth are compared in Table 4.6, and the results of the multiple correlation analysis are shown in Table 4.7.

Table 4.6. Comparison of summer and winter averages.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Summer (April - September)</th>
<th>Winter (October - March)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of obs.</td>
<td>Mean</td>
</tr>
<tr>
<td>222Rn flux (Bq m⁻² h⁻¹)</td>
<td>34</td>
<td>49.0</td>
</tr>
<tr>
<td>220Rn flux (Bq m⁻² h⁻¹)</td>
<td>34</td>
<td>1713</td>
</tr>
<tr>
<td>Soil moisture (m³ m⁻³)</td>
<td>26</td>
<td>0.32</td>
</tr>
<tr>
<td>Water table depth (m)</td>
<td>34</td>
<td>-0.59</td>
</tr>
</tbody>
</table>

**222Rn flux**

The 222Rn flux was approximately normally distributed, with a mean of 42.4 Bq m⁻² h⁻¹ and standard deviation of 16.6 Bq m⁻² h⁻¹ (Table 4.5). The mean flux for the summer months was ~30% greater than the mean flux for the winter months (Table 4.6). The largest 222Rn flux recorded was 92.4 ± 10.6 Bq m⁻² h⁻¹. This was measured on 24th April, towards the end of a period where there had been a general increase in the 222Rn flux, coinciding with a fall in the water table (Fig. 4.6b). The water table level continued to fall after this point in time, and eventually was below the soil-bedrock interface (0.72 m depth); however, this fall was not accompanied by a further increase in the 222Rn flux. Large 222Rn fluxes were also recorded on 19th Oct (79.4 ± 5.3 Bq m⁻² h⁻¹), 28th June (75.6 ± 9.5 Bq m⁻² h⁻¹), 26th Sept (86.6 ± 4.3 Bq m⁻² h⁻¹), and 12th Nov (82.3 ± 6.5 Bq m⁻² h⁻¹). These fluxes were all recorded after the soil had begun to dry out after heavy rainfall, suggesting that there had been an accumulation of 222Rn in
Table 4.7. Correlation matrix for the seasonal study.

<table>
<thead>
<tr>
<th></th>
<th>( ^{222}\text{Rn flux} )</th>
<th>( ^{220}\text{Rn flux} )</th>
<th>( ^{222}\text{Rn conc.} )</th>
<th>Soil moisture</th>
<th>Water table depth</th>
<th>Rainfall</th>
<th>Atmos. pressure</th>
<th>Chamber air temp.</th>
<th>Soil surface temp.</th>
<th>Soil temp. at 10cm</th>
<th>Soil temp. diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{222}\text{Rn flux} )</td>
<td>1.00</td>
<td>-0.12</td>
<td>0.04</td>
<td>0.00</td>
<td>0.09</td>
<td>-0.03</td>
<td>0.22</td>
<td>0.27</td>
<td>0.27</td>
<td>0.26</td>
<td>0.05</td>
</tr>
<tr>
<td>( ^{220}\text{Rn flux} )</td>
<td>1.00</td>
<td>0.14</td>
<td>-0.53</td>
<td>0.47</td>
<td>-0.10</td>
<td>0.27</td>
<td>0.31</td>
<td>0.37</td>
<td>0.37</td>
<td>0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>Ambient ( ^{222}\text{Rn concentration} )</td>
<td>1.00</td>
<td>-0.17</td>
<td>0.39</td>
<td>0.16</td>
<td>0.01</td>
<td>0.14</td>
<td>0.16</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>-0.04</td>
</tr>
<tr>
<td>Soil moisture</td>
<td>1.00</td>
<td>-0.59</td>
<td>0.09</td>
<td>-0.12</td>
<td>-0.61</td>
<td>-0.58</td>
<td>-0.56</td>
<td>-0.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water table depth</td>
<td>1.00</td>
<td>0.10</td>
<td>0.06</td>
<td>0.58</td>
<td>0.66</td>
<td>0.65</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainfall</td>
<td>1.00</td>
<td>-0.09</td>
<td>0.12</td>
<td>0.19</td>
<td>0.24</td>
<td>0.24</td>
<td>-0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>1.00</td>
<td>0.11</td>
<td>0.02</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>-0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chamber air temperature</td>
<td>1.00</td>
<td>0.95</td>
<td>0.91</td>
<td>0.13</td>
<td></td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil surface temperature</td>
<td>1.00</td>
<td>0.98</td>
<td>0.76</td>
<td>0.76</td>
<td></td>
<td>0.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil temperature at 10cm</td>
<td>1.00</td>
<td>-0.09</td>
<td></td>
<td></td>
<td></td>
<td>-0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil temperature difference</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
</tr>
</tbody>
</table>
the soil. The smallest $^{222}$Rn flux measured was $11.3 \pm 4.6$ Bq m$^{-2}$ h$^{-1}$, recorded on the 31st Oct, after heavy rainfall the previous day (rainfall amount not recorded). Significantly lower than average $^{222}$Rn fluxes were also recorded on 3rd and 29th Nov 2001 ($16.9 \pm 2$ Bq m$^{-2}$ h$^{-1}$ and $15.8 \pm 3.4$ Bq m$^{-2}$ h$^{-1}$), after 1.3 mm and 1.5 mm of rainfall on the previous day, respectively. Much lower than average fluxes were also recorded on 19th Jan, 12th and 27th Feb, and 2nd March, on all of which days the ground surface was frozen, to a maximum depth of ~5 cm. $^{222}$Rn flux was found to be weakly positively correlated with atmospheric pressure, air temperature, and soil temperature (Table 4.7).

$^{220}$Rn flux

The $^{220}$Rn flux was approximately log-normally distributed. The median flux was 821 Bq m$^{-2}$ h$^{-1}$, and the quartile deviation 593 Bq m$^{-2}$ h$^{-1}$ (Table 4.5). There was a substantial seasonal trend in emissions (Fig. 4.6). The median summer flux was about a factor of two larger than the median winter flux (Table 4.6). As expected, of all variables recorded, $^{220}$Rn flux was found to be most strongly correlated with soil moisture ($r = -0.53$). Maxima and minima in flux generally coincided with peak and minimum soil moisture contents (Fig. 4.6). The largest flux recorded was $5311 \pm 981$ Bq m$^{-2}$ h$^{-1}$, measured on 25th May when the soil surface was very dry (soil moisture content not recorded). The second largest flux ($3986 \pm 685$ Bq m$^{-2}$ h$^{-1}$), which was recorded on 19th Sept, coincided with the lowest soil moisture value recorded ($0.21$ m$^3$ m$^{-3}$). On 30th Nov and 6th Dec 2001 no $^{220}$Rn flux was detected, presumably because of the relatively high soil moisture levels, which were 0.36 and 0.37 m$^3$ m$^{-3}$, respectively. Very small fluxes were recorded on 7th Dec ($30 \pm 53$ Bq m$^{-2}$ h$^{-1}$) and 18th May ($45 \pm 60$ Bq m$^{-2}$ h$^{-1}$). In each case rainfall had occurred on the previous day or days. The median $^{220}$Rn flux for five soil moisture ranges is shown in Figure 4.7. This figure corresponds very closely to that part of the graph where soil moisture contents are > 8% in Figure 2.5 (§2.3.1, Chapter 2). $^{220}$Rn flux was also found to be moderately
correlated with water table depth ($r = 0.47$), which was correlated with soil moisture ($r = -0.59$), and weakly positively correlated with atmospheric pressure, air temperature, and soil temperature (Table 4.7).

![Figure 4.7](https://example.com/figure47.png)

**Figure 4.7.** Median $^{220}$Rn fluxes for five soil moisture ranges. The soil moisture ranges and number of observations, $n$, were: 0.2-0.25 ($n=3$), 0.25-0.3 ($n=8$), 0.3-0.35 ($n=19$), 0.35-0.4 ($n=32$), and 0.4-0.45 ($n=6$). Error bars are the quartile deviation.

**Soil freezing and snow cover**

Mean $^{222}$Rn fluxes and median $^{220}$Rn fluxes for when the soil surface was frozen (to a maximum depth of ~ 5 cm) and unfrozen are shown in Table 4.8. Values are for the winter months only (October – March). The mean $^{222}$Rn flux for all days when the ground surface was frozen was 28.4 Bq m$^{-2}$ h$^{-1}$ and the median $^{220}$Rn flux was 745 Bq m$^{-2}$ h$^{-1}$. For normal (i.e. unfrozen) conditions the mean $^{222}$Rn flux was 41.1 Bq m$^{-2}$ h$^{-1}$ and the median $^{220}$Rn flux was 617 Bq m$^{-2}$ h$^{-1}$. Thus, the mean $^{222}$Rn
flux for when the soil surface was frozen was about a third lower than the mean flux for normal conditions, but conversely the corresponding median $^{220}$Rn flux was $\sim 20\%$ greater. The correlation between $^{222}$Rn and $^{220}$Rn for when the ground surface was frozen was $r = -0.23$, and for when it was unfrozen it was $r = -0.12$.

Table 4.8. Mean and median $^{222}$Rn and $^{220}$Rn fluxes when the soil was frozen and unfrozen for the winter months (October – March).

<table>
<thead>
<tr>
<th></th>
<th>Frozen</th>
<th>Not frozen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of obs. Mean Median Std. dev. Skewness</td>
<td>No. of obs. Mean Median Std. dev. Skewness</td>
</tr>
<tr>
<td>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>11 28.4 24.5 10.7 0.78</td>
<td>48 41.0 38.6 15.6 0.63</td>
</tr>
<tr>
<td>$^{220}$Rn flux (Bq m$^{-2}$ s$^{-1}$)</td>
<td>11 878 745 681 1.58</td>
<td>47 775 617 657 1.17</td>
</tr>
</tbody>
</table>

$^{222}$Rn and $^{220}$Rn fluxes measured between 12th Jan and 18th March 2001 are shown in Figure 4.8. This period was characterised by short spells of frost, in-between which the ground completely thawed. Between 27th Feb and 7th March there was at least 4 cm of snow cover, as well as a frozen soil surface layer (5 cm depth at the most). All except one of the $^{222}$Rn fluxes measured when the ground surface was frozen were smaller than the winter mean $^{222}$Rn flux for unfrozen conditions (Fig. 4.8), and the mean $^{222}$Rn flux when the ground was frozen was significantly ($p < 0.05$) lower than the mean $^{222}$Rn flux from unfrozen ground. $^{220}$Rn fluxes measured when the ground was frozen were either above, below, or close to the median flux for unfrozen conditions, but lower $^{220}$Rn fluxes were observed when the snow cover became icy at the surface on 2nd March (Fig. 4.8). Between 9th and 23rd Feb the $^{220}$Rn flux increased by a factor of 3 of 4, and between 9th and 16th the $^{222}$Rn flux approximately doubled. This reason for this is not known, but it is possible that it was partly caused by physical disruption of the soil aggregates by freeze-thaw action, thus allowing more radon to escape (especially $^{220}$Rn, because of its
shallower. The correlation coefficient for $^{222}$Rn and $^{220}$Rn for this period was -0.38 ($n = 9$).

![Figure 4.8](image-url)  

**Figure 4.8.** $^{222}$Rn and $^{220}$Rn fluxes measured between 12th January and 16th March 2001. The dashed lines are winter (Oct-March) mean ($^{222}$Rn) and median ($^{220}$Rn) fluxes for when the ground was not frozen. On 2nd March the snow surface was icy due to re-freezing after thawing.

### 4.3.3 Soil monolith study

$^{222}$Rn fluxes measured from the soil monolith at mean water table depths of between 0.06 m and 0.46 cm are shown with the water table depth in Figure 4.9. Summary statistics are given in Table 4.9. $^{222}$Rn fluxes ranged from zero to ~ 30 Bq m$^{-2}$ h$^{-1}$, and, as expected, showed a general trend of a decreasing flux with decreasing water table
Chapter 4 Temporal studies of $^{222}$Rn and $^{220}$Rn flux

Figure 4.9. $^{222}$Rn fluxes measured from a soil monolith at five water table depths.

Table 4.9. Summary statistics for the soil monolith experiment.

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs</th>
<th>Mean</th>
<th>Std. dev.</th>
<th>Median</th>
<th>Quart. dev</th>
<th>Min.</th>
<th>Max.</th>
<th>Skewness</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>49</td>
<td>8.2</td>
<td>6.6</td>
<td>6.9</td>
<td>4.9</td>
<td>-3.3</td>
<td>27.3</td>
<td>0.78</td>
<td>81</td>
</tr>
<tr>
<td>Water table depth (m)</td>
<td>49</td>
<td>0.27</td>
<td>0.15</td>
<td>0.26</td>
<td>0.10</td>
<td>0.06</td>
<td>0.48</td>
<td>0.01</td>
<td>56</td>
</tr>
<tr>
<td>Change in water table depth (%)</td>
<td>48</td>
<td>6.2</td>
<td>11.3</td>
<td>1.4</td>
<td>4.0</td>
<td>0.0</td>
<td>60.0</td>
<td>3.00</td>
<td>181</td>
</tr>
<tr>
<td>Soil moisture (m$^3$ m$^{-3}$)</td>
<td>45</td>
<td>0.30</td>
<td>0.11</td>
<td>0.29</td>
<td>0.12</td>
<td>0.16</td>
<td>0.46</td>
<td>0.14</td>
<td>37</td>
</tr>
<tr>
<td>Atmospheric pressure (hPa)</td>
<td>49</td>
<td>995</td>
<td>14.9</td>
<td>999</td>
<td>8.5</td>
<td>944</td>
<td>1021</td>
<td>-0.90</td>
<td>2</td>
</tr>
<tr>
<td>Air temperature inside chamber (°C)</td>
<td>49</td>
<td>23.4</td>
<td>1.4</td>
<td>23.0</td>
<td>0.5</td>
<td>20.0</td>
<td>27.0</td>
<td>0.30</td>
<td>6</td>
</tr>
<tr>
<td>Soil surface temperature (°C)</td>
<td>46</td>
<td>19.4</td>
<td>1.2</td>
<td>19.0</td>
<td>0.5</td>
<td>17</td>
<td>22</td>
<td>0.30</td>
<td>6</td>
</tr>
<tr>
<td>Soil temperature at 10cm (°C)</td>
<td>46</td>
<td>19.2</td>
<td>1.0</td>
<td>19.0</td>
<td>0.5</td>
<td>17.0</td>
<td>22.0</td>
<td>0.55</td>
<td>5</td>
</tr>
</tbody>
</table>

*Change in water table depth is the change relative to the value recorded before the previous flux measurement. Skewness after log-e transformation was -0.30.
Chapter 4  Temporal studies of $^{222}$Rn and $^{220}$Rn flux

depth. The correlation coefficient for $^{222}$Rn flux and water table depth was -0.67 ($p < 0.01$). $^{222}$Rn flux also showed a moderate correlation with soil moisture ($r = -0.57$, $p < 0.01$), which was strongly correlated with water table depth ($r = -0.95$, $p < 0.01$). No significant correlation was found with any other variable. Figure 4.10 shows the mean $^{222}$Rn flux as a function of mean water table depth for the five water table depth ranges. The correlation coefficient was -0.98.

![Figure 4.10. Mean $^{222}$Rn flux vs mean water table depth. Error bars are the standard deviation.](image)

4.4 Discussion
4.4.1 Factors controlling the temporal variability of $^{222}$Rn and $^{220}$Rn fluxes

Soil moisture and rainfall

Soil moisture content was the most important factor affecting the $^{220}$Rn flux ($r = -0.53$), as expected, but no correlation was found with $^{222}$Rn flux (Table 4.7). Given that the soil moisture measurements were only for the top 8 cm of soil, a much stronger correlation would be expected for $^{220}$Rn flux and soil moisture content, however, because the soil moisture measurements integrate over the entire depth of soil producing
220Rn which escapes to the atmosphere, but only over a portion of that for 222Rn (§2.2.2). Also, given its much shorter half-life, the 220Rn flux is more susceptible to changes in its diffusivity in the soil ($D_c$) than 222Rn. Changes in the saturation of the soil surface layer due to wetting and drying of the soil after rainfall were clearly important for the 222Rn flux on some occasions, however. For example, on 20th July 2001 rainfall caused a total reduction in emissions (Fig. 4.2), and, during the seasonal study, much smaller than average fluxes were recorded on 31st Oct, 3rd Nov and 29th Nov 2001, after heavy rainfall on the previous days (Fig. 4.6; §4.3.2). No clear relationship was found between the amount of rainfall and the degree of reduction in flux, however. For example, during the summer short-term study, a total suppression in the 222Rn flux was observed after only 2 mm of rain on the 20th, but 8 mm of rainfall on the 12th did not cause as large a reduction in flux (Fig. 4.2). Given the dry spell of weather between the 15th and 20th, it is likely that the soil would have been drier on the 20th than on the 12th. Thus, the total reduction in flux observed on the 20th was more probably caused by the intensity of the 2 mm of rainfall on this date, with water temporarily collecting on the soil surface and forming a barrier to diffusion, rather than to the change in soil profile water content.

When rain caused complete interruption in the 222Rn flux, the flux was found to recover within 24 hours (Fig. 4.2). The length of time which the flux takes to recover to pre-rainfall levels after such an event will depend on how close to saturation the soil is prior to the rainfall, the nature of the soil surface (e.g. compacted, cracked), the amount and type of vegetation (if any), and the local microclimate (e.g. amount of sunshine, shelter). Ussler et al. (1994) noted that the 222Rn flux recovered in a matter of hours after heavy rainfall at a site in a dry upland open-canopy lichen-spruce woodland. Other studies have reported recovery times of less than two days (Megumi and Mamunro, 1973; Ishimori et al., 1998). Some authors have reported much higher than average fluxes after the soil had begun to dry out after heavy rainfall had caused a complete interruption in flux (e.g. Ishimori et al., 1998; Ferry et al., 2001). During the
seasonal study, much higher than average $^{222}\text{Rn}$ fluxes were sometimes observed after
there had been such an interruption in emissions, but this was not always the case. For
example, the flux recovered gradually on 20th July 2001 (Fig. 4.2), but much higher
than average $^{222}\text{Rn}$ fluxes were recorded on 19th Oct (79.4 Bq m$^{-2}$ h$^{-1}$), 28th Jun (75.6
Bq m$^{-2}$ h$^{-1}$), 26th Sep (86.6 Bq m$^{-2}$ h$^{-1}$) and 12th Nov (82.3 Bq m$^{-2}$ h$^{-1}$). These fluxes are
78-104% higher than the mean flux of 42.4 Bq m$^{-2}$ h$^{-1}$, and 82-109% higher than the
mean of the five preceding flux measurements in each case. Again, the length of the
recovery time will be site-specific, depending on the type of soil and type of vegetation,
if any, the local meteorological conditions, and the degree of saturation of the soil prior
to rainfall. The concurrently measured $^{220}\text{Rn}$ flux was not found to be higher than
average on any of these occasions, as would be expected, given its short half-life.

Water table depth
In line with the observations made by Conen and Robertson (2002) (Fig. 2, Appendix
A), the soil monolith study demonstrated that water table depth is an important factor
controlling $^{222}\text{Rn}$ emissions. The coefficient of determination for the full dataset was
45%, and for the mean fluxes and mean water table depths it was 96% (Figure 4.10). On
the whole, $z^w$ was not found to be an important factor affecting $^{222}\text{Rn}$ flux during the
seasonal study ($r = 0.09$), but it did appear to be important during the period 12th March
- 4th April, when there was a general increase in $^{222}\text{Rn}$ flux from ~ 35 Bq m$^{-2}$ h$^{-1}$ to
~ 60 Bq m$^{-2}$ h$^{-1}$, when $z^w$ dropped from 0.20 m to 0.45 m below the surface (Fig. 4.6).
This suggests that $z^w < z^d$ for a significant part of the study, and thus was not an
important factor (§2.3.1). This conjecture is supported by the fact that, after the general
increase in flux over the period 12th March - 4th April, the $^{222}\text{Rn}$ flux did not increase
any further when $z^w$ dropped from 0.45 m depth to below bedrock depth (0.72 m).
Further, a moderate correlation was found between $^{222}\text{Rn}$ flux and water table depth for
all data with $z^w > 0.45$ m ($r = -0.49$, $p < 0.05$). Water table depth was not an important
factor for the $^{220}$Rn flux, as expected (the correlation being in the wrong direction - Table 4.7).

**Atmospheric pressure**

Atmospheric pressure was not found to be an important factor affecting $^{222}$Rn and $^{220}$Rn fluxes in any of the studies carried out, as expected. Although a weak correlation was found between atmospheric pressure and $^{222}$Rn and $^{220}$Rn flux for all field studies (§4.3.1; Table 4.7), this was in the wrong direction (positive) to suggest that atmospheric pressure was an important factor. No correlation was found between $^{222}$Rn flux and the change in atmospheric pressure either (§4.3.1). Although variations in atmospheric pressure have been shown to cause significant variations in the $^{222}$Rn flux from soils with a high air-filled porosity or which are fractured (e.g. Clements and Wilkening, 1974; Schery and Gaeddert, 1982; Duenas and Fernandez, 1987), atmospheric pressure is generally of minor importance for moist soils (Schery et al., 1982; Schubert and Schulz, 2002). Changes in partial pressures in the soil gas are also unlikely to be important, as, even in very biologically active soils, the diffusivity of radon in air will change little over the range of CO$_2$ concentrations commonly found in soil air.

**Soil temperature**

Soil temperature was found to be weakly positively correlated with $^{222}$Rn flux and $^{220}$Rn flux during the short-term summer and seasonal studies (§4.3.1; Table 4.7), as has been noted by several other authors (e.g. Schery et al., 1989). Given that enhanced diffusion coefficients and thermal expansion of the soil air are generally of minor importance over the range of temperatures found in the environment (Schery et al., 1989), it is unlikely that this weak correlation reflects any enhanced transport effect, but it is possible that it may reflect a small effect due to the decreased solubility of radon at higher temperatures. Between the temperature range of 0°C and 10°C, the solubility of $^{222}$Rn in water decreases by ~15% (§2.2.1). Thus, a decrease in temperature would cause an increase
in soil gas concentrations, which would enhance the radon flux. This enhancement will be small, however, and, as an increase in soil temperature will tend to reduce the soil moisture content, the correlation between radon flux and soil temperature will also reflect that between soil temperature and soil moisture (r = -0.58). However, given that no correlation was found between $^{222}$Rn flux and soil moisture, and yet a correlation was found with soil temperature (r = 0.27), this suggests that the correlation between radon fluxes and temperature could reflect a small effect due to, for example, decreased solubility or enhanced diffusion. As the relationship between solubility and temperature is non-linear, this effect is more important in the lower temperature range. The weak negative correlation between $^{222}$Rn flux and soil temperature (r = -0.26) for the short-term winter suggests a small effect due to freezing of the soil surface. The effects of soil freezing are discussed below.

Soil freezing

During the short-term winter study, freezing of the top 5-6 cm of the soil had no effect on the $^{222}$Rn flux (Table 4.4, Fig 4.5). Slightly lower than average fluxes were observed towards the end of the thawing period, however, probably due to an increase in the soil moisture content, caused by melting of the ice crystals which had grown on the soil surface. In the case of the seasonal study, however, the mean $^{222}$Rn flux for when the ground surface was frozen (to a maximum depth of 5 cm) was about one-third less than the mean $^{222}$Rn flux for when the soil surface was unfrozen, but no reduction was observed in the concurrently measured $^{220}$Rn flux (the median flux for frozen conditions was ~ 20% higher than for frozen conditions) (Table 4.9; Fig. 4.8). The significant increase in both the $^{222}$Rn and $^{220}$Rn flux observed after the 9th, after the ground surface had been frozen on the 7th and 8th (Fig. 4.8), was most likely caused by physical disruption of the soil aggregates by freeze-thaw action, which would have enhanced the emanating fraction. Given the much shorter half-life of $^{220}$Rn compared to $^{222}$Rn, freezing of the ground surface having a more significant effect on $^{222}$Rn flux than $^{220}$Rn.
flux is contrary to what would be expected, as, for a frozen surface layer of ~ 5 cm, the reduction in $D_e$ caused by expansion of the soil water on freezing would affect a much larger proportion (probably all) of the depth of soil which produces the radon that escapes to the atmosphere. Using Equation (2.5), for a soil moisture content of 0.34 m$^3$ m$^{-3}$ (the value recorded on the 10th January) the reduction in $D_e$ as a result of the soil water freezing would be ~ 18% (for $\varepsilon_T = 0.585$, and assuming a 10% expansion in the volume of the water on freezing). This would translate to only a small change in flux, however, even for situations with soil gas concentrations several orders of magnitude higher than the atmospheric concentration. For example, assuming an increase in soil gas concentrations in the frozen layer of a similar proportion to the reduction in $D_e$ and no change in the atmospheric concentration, from Equation (2.1), for soil gas concentrations four orders of magnitude higher than the atmospheric concentration, the reduction in $^{222}$Rn flux expected due to an 18% reduction in $D_e$ would be < 2.5%. Although the relative reduction in $D_e$ (and thus flux) will be greater at higher soil moisture contents (Figure 4.11), as $D_e$ decreases non-linearly with increasing soil moisture content (Fig. 2.3, §2.2.2), the absolute reduction in flux will be small at higher soil moisture contents. Thus, freezing of the soil should only result in a notable reduction in radon emissions if a significant barrier to diffusion forms, for example, if a closed ice layer develops on the soil surface, or lenses form within the soil. The much lower than average $^{222}$Rn fluxes observed when the soil was frozen during the seasonal study were probably due to the chamber not being sealed properly.
Figure 4.11. The relative reduction in the $^{222}$Rn effective diffusion coefficient ($D_e$) as a result of the soil water freezing. Values were calculated using Equation 2.5, and assuming a 10% expansion in volume.

Snow cover

The $^{222}$Rn and $^{220}$Rn fluxes measured when there was a snow cover of 3-4 cm depth (in addition to a frozen soil surface layer of 5 cm depth at maximum) were all within the range, or greater than, the fluxes measured when the soil surface was frozen (but had no snow cover) in the previous weeks (Figure 4.8). This observation would suggest that the snow cover did not have a significant effect on emissions, as would be expected, given the relatively large porosity and low tortuosity of fresh snow compared to soil. On 2nd March, however, when the snow surface became icy after re-freezing of thawed snow, both the $^{222}$Rn and $^{220}$Rn fluxes were significantly lower than the immediately preceding flux in each case (fluxes were ~ 66% and 20% lower, respectively). Besides a reduction in the diffusivity of the snow caused by melting and re-freezing, this decrease (which we would expect to be greater for $^{220}$Rn because of its shorter half-life) could also have been
caused by an increase in soil moisture content. Yamazawa et al. have observed a decrease in $^{222}\text{Rn}$ flux as a result of increased soil moisture at a mountain site in Japan (J. Moriizumi, pers. comm.), whilst Moriizumi et al., (2004) found a dry snow cover to have no effect on $^{222}\text{Rn}$ emissions at a site in western Siberia. Thus, when considering the effect of snow cover on flux, in addition to the physical properties of the snow which affect the transport of radon though the soil (e.g. porosity and tortuosity), the effect of thawing on the soil moisture content also needs to be considered. Because of its much shorter half-life, the depth of the snow cover will also be important for $^{220}\text{Rn}$ flux, as indicated by the fact that Kataoka et al., (2003) observed snow cover to have no effect on $^{222}\text{Rn}$ concentrations, but did observe a reduction in concentrations of $^{212}\text{Pb}$ (a daughter product of $^{220}\text{Rn}$).

4.4.2 Variability of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ fluxes

Short-term and diurnal variability

Coefficients of variation (CVs) for $^{222}\text{Rn}$ flux for the two short-term studies were 33% and 24% for the summer and winter studies, respectively (Tables 4.1 and 4.3), and, for the summer study excluding the period when heavy rainfall caused a marked reduction in emissions on 21-22nd July, the CV was 24%. This level of variability is much less than that typically observed on this time-scale for some other gases emitted or taken-up by the soil, for example coefficients of variation for the $\text{N}_2\text{O}$ fluxes reported by Smith and Dobbie (2001) range from 77 to 334%. CVs for $^{222}\text{Rn}$ and $^{220}\text{Rn}$ for the seasonal data set were 39% and 89%, respectively, and were higher for the winter months than for the summer months because of more frequent rainfall during the winter (Table 4.6; Fig. 4.6).

The analysis of a small data set ($n = 4$) of $^{222}\text{Rn}$ fluxes measured on days when there was no rainfall suggests that there could be a significant diurnal trend of an afternoon maximum and morning minimum in $^{222}\text{Rn}$ emissions at this site on days unaffected by
Temporal studies of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ flux

rainfall (Fig. 4.3; Table 4.2). The mean $^{222}\text{Rn}$ flux for the morning period was 20% lower ($p < 0.05$) than the mean $^{222}\text{Rn}$ flux for the afternoon, and the amplitude was 12.5 Bq m$^{-2}$ h$^{-1}$, which is $\sim 40\%$ of the mean $^{222}\text{Rn}$ flux for this period. This pattern in emissions is very similar to that observed by some others; for example, Kojima (1998) observed a diurnal trend in $^{222}\text{Rn}$ flux of typically 20%, with a maximum in emissions at $\sim 1500\text{h}$ and the minimum at $\sim 0600\text{h}$. He found this pattern corresponded to the diurnal cycle in the difference between the pressure at the soil surface and at 1 m depth, and thus reflected the diurnal variation in pressure differences due to atmospheric turbulence. Schery et al., (1984) also observed a similar diurnal pattern in $^{222}\text{Rn}$ emissions from a gravelly sandy loam soil and attributed this to the diurnal pressure variations. However, given that variations in atmospheric pressure are not expected to be a major factor affecting radon transport in moist soils (Schubert and Schulz, 2002), and that temperature is not a major factor over the range of temperatures encountered in the environment (Schery et al., 1984), the diurnal variation in flux observed at this site is probably more likely to be related to diurnal variations in soil moisture content and water table depth, as a result of the diurnal cycle in evapotranspiration (e.g. Scott et al., 2004).

Seasonal variability

The seasonal variability in $^{222}\text{Rn}$ and $^{220}\text{Rn}$ emissions observed at the Botany garden site was within the range of variability reported by others (e.g. Schüssler, 1996; Whittlestone et al., 1996; Whittlestone et al., 1998). The mean summer $^{222}\text{Rn}$ flux was $\sim 30\%$ higher than the winter mean, and the median summer $^{220}\text{Rn}$ flux was a factor of 2 larger than the winter median (Fig. 4.6 and Table 4.6). Whittlestone et al., (1998) also found the seasonality in $^{220}\text{Rn}$ flux to be much greater than that $^{222}\text{Rn}$. This reflects the fact that the $^{220}\text{Rn}$ flux is much more susceptible to variations in surface soil moisture content caused by rainfall, because of its much shorter diffusion length, and hence its much stronger correlation with the surface soil moisture content than that for $^{222}\text{Rn}$ flux and
soil moisture content (Table 4.7). Considering monthly mean fluxes, the amplitude of the seasonality in $^{222}$Rn flux was 36 Bq m$^{-2}$ h$^{-1}$, which is $\sim$ 80\% of the mean flux. The $^{220}$Rn flux had an amplitude of 2732 Bq m$^{-2}$ h$^{-1}$, which is 285\% of the median flux. In the case of $^{222}$Rn, this is less than values typically observed for some other gases emitted or taken up by the soil on this time-scale, for example the amplitude in the seasonal cycle in CH$_4$ emissions from wetlands is typically 100-150\% of the annual mean flux (Chang and Yang, 2003).

4.5 Summary and conclusions

- Soil moisture content is the most important factor affecting radon emissions. If the depth to the water table is less than the relaxation depth, the water table depth is also an important factor for $^{222}$Rn flux, but, because of its much shorter diffusion length, variations in water table depth are unlikely to be important for $^{220}$Rn flux.

- Rainfall may temporarily completely suppress radon emissions, as a result of occlusion of the soil pores, or the formation of a water barrier to diffusion at the surface. Much larger than average fluxes may occur afterwards, due to an accumulation in the soil, however, if the soil dries out slowly, this is not always the case.

- Variations in atmospheric pressure are of minor importance for moist soils, and soil temperature is not an important factor over the range of temperatures found in the environment.

- Freezing of the soil will only result in a significant reduction in emissions if a substantial barrier to diffusion forms e.g. a closed ice layer on the soil surface, or lenses within the soil.
The effect of snow cover on radon emissions will depend on its physical characteristics (porosity, tortuosity) and the degree of waterlogging of the soil caused by snow melt. The depth of snow cover will also be important for $^{220}$Rn. A fresh and dry snow cover is likely to have minimum impact on the $^{222}$Rn flux, but, depending on its depth, may affect the $^{220}$Rn flux.

$^{222}$Rn emissions are typically much less variable than those of some other gases emitted from the soil e.g. $N_2O$ and $CH_4$.

Radon emissions may exhibit a diurnal pattern in emissions of a maximum in flux during the day and minimum in the morning as a result of the typical diurnal pattern in atmospheric pressure variations, but this could also be caused by diurnal variations in soil moisture content and water table depth due to the diurnal pattern in evapotranspiration.
Chapter 5

Spatial studies of $^{222}\text{Rn}$ flux

5.1 Introduction

Despite the large and widespread interest in $^{222}\text{Rn}$ over the past few decades, there have been only a few systematic surveys of terrestrial emissions of $^{222}\text{Rn}$ (Schery et al., 1989; Graustein and Turekian, 1990; Whittlestone et al., 1996, 1998; Nielson et al., 1996; Jennings, 2003). $^{222}\text{Rn}$ emissions have been found to be logarithmically distributed on the regional scale (Schery et al., 1989; Nielson et al., 1996), and their variability to be strongly related to the $^{226}\text{Ra}$ content of the soil, and thus its parent material (Keller and Schütz, 1988; Hafez et al., 1991; Nielson et al., 1996; Dueñas et al., 1997; Ielsch et al., 2001). On a more local scale, soil texture and soil moisture content are the most important factors controlling the spatial variability of emissions (Dörr and Männich, 1990).

In this Chapter the results of studies carried out to investigate the spatial variability of $^{222}\text{Rn}$ emissions at the local, regional and global scales, and the factors controlling this variability, are presented and discussed. Studies at the local scale were a random sampling study carried out in an approximately 20 m by 20 m area, and a 200 m-length transect study. $\text{N}_2\text{O}$ fluxes were also measured, in order to compare the variability of emissions of this biogenically produced gas with those of $^{222}\text{Rn}$, which originate by a purely physical process. Additionally, geostatistical methods of analysis (experimental variograms) have been used to investigate the spatial dependence and structure of the spatial variability of $^{222}\text{Rn}$ and $\text{N}_2\text{O}$ emissions. Geostatistics provide powerful tools for
investigating the spatial variability of environmental properties which vary continuously in space (Webster and Oliver, 2001), but they do not appear to have been used in any studies of radon flux. However, they have been applied in a small number of studies concerned with the spatial variability of \(^{222}\text{Rn}\) in soil gas (Badr et al., 1989; Oliver and Badr, 1995; Oliver and Khayrat, 2001).

The investigation of the spatial variability in \(^{222}\text{Rn}\) emissions at the regional scale has focused on North Britain, an area where soils are expected to vary widely in their \(^{226}\text{Ra}\) content, because of the fairly complex geology of this region. \(^{222}\text{Rn}\) flux measurements were made at 15 sites of differing soil type and parent material, and have been related to the \(^{226}\text{Ra}\) content and some physical properties of the soil, such as texture and depth. The ‘in-situ’ terrestrial gamma dose rate was also measured at a number of these sites. Gamma radiation has been found to correlate reasonably well with \(^{222}\text{Rn}\) flux (Schery et al., 1989; Nielson et al., 1996) and indoor radon concentrations (Duval and Otton, 1990; Poncella et al., 2004), but it does not appear to have been used to predict \(^{222}\text{Rn}\) emissions. The use of gamma radiation measurements as an accurate proxy for \(^{222}\text{Rn}\) flux is limited by the fact that the relative contributions to the gamma dose rate by the various gamma-emitting radionuclides (mainly \(^{40}\text{K}\), and \(^{238}\text{U}\) and \(^{232}\text{Th}\) series nuclides) are spatially variable. However, given the current lack of information on the spatial distribution of \(^{222}\text{Rn}\) emissions, and that gamma dose rate is routinely monitored across large parts of the world as part of national radiation surveillance networks which have been set-up to detect dangerous levels of radiation in the event of a nuclear accidents, this correlation could provide a cheap and effective means of producing a spatial description of \(^{222}\text{Rn}\) emissions on the regional-scale, especially for regions where the monitoring network is quite dense.

Global-scale patterns in \(^{222}\text{Rn}\) emissions have been investigated by examining the latitudinal and longitudinal distribution of large-scale indirect \(^{222}\text{Rn}\) flux measurements.
published in the literature (Conen and Robertson, 2002/Appendix A). Indirect $^{222}$Rn flux estimates based on atmospheric profiles of $^{222}$Rn or boundary layer budgets are useful for investigating large-scale trends in emissions as they integrate over much larger areas than chamber-based studies, and thus may indicate large-scale trends in emissions, such as variations due to increased snow and ice cover at high latitudes, or to the large area of the Eurasian continent covered by wetlands.

5.2 Methods

5.2.1 Local-scale studies

Study area

Measurements were carried out on a sheep-grazed grass field at the Bush Estate, approximately 10 miles south of Edinburgh, Scotland. The soil at this site is an imperfectly drained clay loam of the Macmerry series (a gleyic cambisol). The parent material is Carboniferous sediment, which is overlain with boulder clay.

Field measurements

Two studies were carried out: 1) a random sampling study in which flux measurements were made at eight randomly chosen locations in an approximately 20 m by 20 m area, and 2) a transect study in which measurements were made at 4 m intervals along a 200 m long transect. The random sampling study was carried out on 4th April 2001, and the transect study was carried out over two days in December 2001, during a period of dry and stable (cold and overcast) weather conditions. $^{222}$Rn fluxes were measured by the grab-sampling method (§3.3.4), using 40 cm-diameter chambers (Fig. 3.8a, §3.3.2). N$_2$O sampling and analysis was carried out as described in Dobbie and Smith (2003). A brief description will be given here. After a closure time of 40-60 min and prior to sampling the chamber headspace for $^{222}$Rn, air samples were collected into 20 ml crimp-top glass vials using a hand-operated pump. In order to ensure effective flushing, the vials were repeatedly evacuated and filled with air from the chamber. Ambient gas
samples (two replicates) were taken prior to closure of the chambers. \(\text{N}_2\text{O}\) concentrations were determined using a gas chromatograph fitted with an electron capture detector and equipped with an automated sample injector system.

**Geostatistical analysis**

Experimental variograms were computed using the following equation:

\[
\gamma(d) = \frac{1}{2(N-d)} \sum_{i=1}^{N-d} (\phi_i - \phi_{i+d})^2
\]

(5.1)

where \(\gamma\) is the semivariance, \(d\) is the lag distance, \(\phi\) is the measured variable, and \(i = 1, 2, \ldots, N\) (Webster and Oliver, 2001). Data were checked for the observed trends by fitting linear and quadratic lines on the coordinates. Variograms show the semivariance (essentially half of the difference between pairs of values squared) of a variable as a function of the separation distance between two points, and thus indicate the correlation range, or limit of spatial dependence. The shape of the experimental variogram may take many forms, depending on the data and sampling interval used. Ideally, the semivariance increases with distance between sample locations, rising to a more or less constant value – the ‘sill’ – at a given separation or lag distance, which is called the range of spatial dependence. Samples separated by distances closer than the range are spatially dependent or correlated. In theory, the semivariogram should start from zero, but experimental variograms generally do not, showing a random or ‘nugget’ variance which cannot be detected (below the shortest lag distance) or which is due to measurement error (Webster and Oliver, 2001).
5.2.2 Regional-scale study

Study area

\(^{222}\)Rn flux measurements were made at 15 sites of differing soil type and parent material in North Britain between October 2000 and August 2003. The location, soil classification, and parent material at each site are given in Table 5.1. Four of these sites (labelled 1-4) were locations where \(^{222}\)Rn flux measurements had been made as part of studies of the temporal variability in emissions (Chapter 4; Conen and Robertson, 2002/Appendix A), and the remaining 11 were on the Shetland Islands (sites 5-15). Shetland was chosen as a detailed study area because of its diverse geology within a relatively small area.

Field measurements

Measurements were made at sites 1-4 between Oct 2000 and Dec 2001, and those at sites 5-15 during July 2002 and August 2003. \(^{222}\)Rn fluxes were measured using the continuous monitoring method (§3.3.3) at sites 1 and 5-15, and the grab-sampling method at sites 2-4. At sites 1-4 the 40-cm diameter chamber was used, and at sites 5-15, the 25 cm-diameter was used (Fig. 3.8, §3.3.2). During the August 2003 campaign, the terrestrial gamma dose rate was also measured, using a Bicron Scalar-Ratemeter 2” x 2” NaI(Tl) crystal and photomultiplier, coupled to a Rainbow Multi-Channel Analyser (Health Physics Instruments). The detector was mounted at 1 m above the ground on a tripod. Two 10-minute spectra were collected for each \(^{222}\)Rn flux measurement: one at the start of the accumulation period, and one at the end. At the end of measurements the data were transferred from the MCA to a PC for storage. Calibration and processing were carried out at the Scottish Universities Environmental Research Centre (SUERC). The detector was calibrated using concrete calibration pads spiked with \(^{238}\)U, \(^{232}\)Th and \(^{40}\)K (and one blank), and processing was carried out using software developed by researchers at SUERC. A more detailed description of the instrumentation, data processing, and calibration procedure can be found in Tyler (1994).
Table 5.1. Location, soil type and parent material of the sites where $^{222}$Rn flux measurements were made.

<table>
<thead>
<tr>
<th>Site</th>
<th>Lat. (°N)</th>
<th>Long. (°W)</th>
<th>Soil type</th>
<th>Bedrock</th>
<th>Quaternary sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Botany Garden (1)</td>
<td>55°55'17&quot;</td>
<td>3°10'5&quot;</td>
<td>Gley</td>
<td>Sandstone</td>
<td>Boulder clay</td>
</tr>
<tr>
<td>Flotterstone (2)</td>
<td>55°54'22&quot;</td>
<td>3°13'25&quot;</td>
<td>Gley</td>
<td>Limestone</td>
<td>Boulder clay</td>
</tr>
<tr>
<td>Harwood (3)</td>
<td>55°10'</td>
<td>2°03'</td>
<td>Peat</td>
<td>Limestone</td>
<td></td>
</tr>
<tr>
<td>Griffin (4)</td>
<td>56°36'</td>
<td>3°48'</td>
<td>Peaty Gley</td>
<td>Schist</td>
<td></td>
</tr>
<tr>
<td>Scatness (5)</td>
<td>59°52'27&quot;</td>
<td>1°18'16&quot;</td>
<td>Gley</td>
<td>Sandstone</td>
<td></td>
</tr>
<tr>
<td>Baltasound (6)</td>
<td>60°45'42&quot;</td>
<td>0°51'22&quot;</td>
<td>Gley</td>
<td>Ultrabasic intrusive igneous</td>
<td>Boulder clay and moraine drift</td>
</tr>
<tr>
<td>Belmont (7)</td>
<td>60°41'9&quot;</td>
<td>0°58'4&quot;</td>
<td>Gley</td>
<td>Schist and gneiss</td>
<td>Boulder clay and moraine drift</td>
</tr>
<tr>
<td>Baltasound RS (8)</td>
<td>60°44'16&quot;</td>
<td>0°53'34&quot;</td>
<td>Gley</td>
<td>Ultrabasic intrusive igneous</td>
<td></td>
</tr>
<tr>
<td>Ulsta (9)</td>
<td>60°29'59&quot;</td>
<td>1°09'11&quot;</td>
<td>Peat</td>
<td>Gneiss</td>
<td></td>
</tr>
<tr>
<td>West Yell (10)</td>
<td>60°32'6&quot;</td>
<td>1°10'46&quot;</td>
<td>Peaty gley</td>
<td>Gneiss</td>
<td>Boulder clay and moraine drift</td>
</tr>
<tr>
<td>Noss Hill (11)</td>
<td>59°55'31&quot;</td>
<td>1°20'32&quot;</td>
<td>Peaty gley</td>
<td>Granites</td>
<td>Boulder clay and moraine drift</td>
</tr>
<tr>
<td>Eshaness (12)</td>
<td>60°29'27&quot;</td>
<td>1°37'11&quot;</td>
<td>Peaty gley</td>
<td>Intermediate-basic lava</td>
<td>Boulder clay and moraine drift</td>
</tr>
<tr>
<td>Muckle Roe (13)</td>
<td>60°20'59&quot;</td>
<td>1°24'58&quot;</td>
<td>Peaty gley</td>
<td>Granites</td>
<td></td>
</tr>
<tr>
<td>Virkie (14)</td>
<td>59°53'4&quot;</td>
<td>1°17'54&quot;</td>
<td>Calcareous regosol</td>
<td>Sandstone</td>
<td></td>
</tr>
<tr>
<td>Fetlar (15)</td>
<td>60°30'42&quot;</td>
<td>0°52'45&quot;</td>
<td>Peaty gley</td>
<td>Phyllite</td>
<td>Boulder clay and moraine drift</td>
</tr>
</tbody>
</table>

*Macaulay Institute classification
Chapter 5  

Spatial studies of $^{222}$Rn flux

and Tyler et al. (1996). The gamma dose rate was calculated by two different methods: 1) the integrated count from 450 to 3000 keV, and 2) the integrated energy deposition rate (pJ s$^{-1}$) from 40 to 3000 keV (Sanderson, 2002). The reported values are the average of the two gamma dose rate values calculated by these two methods.

Soil sampling and analysis

At each site of measurement, the soil depth was measured and soil samples were taken. These were analysed for their radionuclide content and particle size distribution. On shallow soils (<0.5 m), six samples were taken by inserting a soil auger to bedrock, and on deeper soils three cores were taken to bedrock depth, using a 6 cm-diameter corer. On returning to the laboratory, the soil samples and cores were air-dried and bulked. For shallow soils the full sample was bulked, but for the soil cores the different horizons were bulked separately. Samples were then dried in an oven at 105°C for 24 hours, and then sieved using 2 mm and 500 µm meshes. Particle size analysis was carried out at the Institute of Earth Science, University of Edinburgh, using a laser granulometer (Coulter LS130), and the radionuclide content of the soil was determined by staff at SUERC, using a germanium (HPGe) detector. The $^{226}$Ra activities reported are equivalent activities, determined from the mean of the $^{214}$Pb (295 keV), $^{214}$Pb (352 keV) and $^{214}$Bi (609 keV) activities. $^{224}$Ra activities reported in this thesis (Chapter 5) are equivalent activities derived from the mean of the $^{212}$Pb (239 keV) and $^{208}$Tl (584 keV) activities.

5.2.3 Global-scale study

$^{222}$Rn fluxes reported in the literature (Turekian et al., 1977; and those studies cited in Conen and Robertson (2002)/Appendix A - Table 1) were gathered, and their distribution with latitude and longitude was investigated for any trends. For direct measurements, the values used were the mean or median $^{222}$Rn flux for each study. The number of individual sites on which these values were based ranged from 1 to > 800,
and the number of samples taken at each site also varied widely (Table 1, Appendix A). Indirect $^{222}$Rn fluxes were the values cited in Turekian et al., (1977).

5.3 Results

5.3.1 Local-scale variability

Random sampling study

$^{222}$Rn and $\text{N}_2\text{O}$ fluxes measured at each chamber location are shown in Figure 5.1, and summary statistics for all variables are given in Table 5.1. $^{222}$Rn fluxes ranged from 6.9 to 18.4 Bq m$^{-2}$ h$^{-1}$, and generally overlapped within the range of uncertainty. The mean $^{222}$Rn flux was 13.2 Bq m$^{-2}$ h$^{-1}$, and the coefficient of variation was 28%. $\text{N}_2\text{O}$ fluxes were all very small and within a similar range (< 5 g $\text{N}_2\text{O-N}$ ha$^{-1}$ d$^{-1}$), except for the flux measured from chamber no. 3. The median $\text{N}_2\text{O}$ flux was 4.1 g $\text{N}_2\text{O-N}$ ha$^{-1}$ d$^{-1}$, and the coefficient of variation 600%.

![Figure 5.1](image)

*Figure 5.1. $^{222}$Rn and $\text{N}_2\text{O}$ fluxes measured from 8 randomly-located chambers in a 20 m by 20 m area of a grazed grass field.*
Table 5.2 Summary statistics for the random sampling study.

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs</th>
<th>Mean</th>
<th>Median</th>
<th>Std. dev.</th>
<th>Min.</th>
<th>Max.</th>
<th>Skewness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}\text{Rn}$ flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>8</td>
<td>13.2</td>
<td>13.8</td>
<td>3.9</td>
<td>6.9</td>
<td>18.4</td>
<td>0.43</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$ flux (g $\text{N}_2\text{O}$ N ha$^{-1}$ d$^{-1}$)</td>
<td>8</td>
<td>12.0</td>
<td>4.1</td>
<td>24.6</td>
<td>0.9</td>
<td>72.7</td>
<td>2.80</td>
</tr>
<tr>
<td>Soil moisture (m$^3$ m$^{-3}$)</td>
<td>8</td>
<td>0.49</td>
<td>0.49</td>
<td>0.02</td>
<td>0.45</td>
<td>0.52</td>
<td>0.19</td>
</tr>
<tr>
<td>Soil surface temperature (°C)</td>
<td>8</td>
<td>7.1</td>
<td>8.0</td>
<td>0.3</td>
<td>7.8</td>
<td>8.7</td>
<td>1.35</td>
</tr>
<tr>
<td>Soil temperature at 10 cm (°C)</td>
<td>8</td>
<td>5.2</td>
<td>5.3</td>
<td>0.1</td>
<td>5.1</td>
<td>5.5</td>
<td>0.74</td>
</tr>
</tbody>
</table>

**Transect study**

$^{222}\text{Rn}$ fluxes, $\text{N}_2\text{O}$ fluxes, and the soil moisture content measured at 4 m intervals along the transect are shown in Figure 5.2. Summary statistics for all variables recorded are given in Table 5.3. All variables were near-normally distributed, except for $\text{N}_2\text{O}$ flux, which was approximately log-normally distributed. $^{222}\text{Rn}$ fluxes ranged from 1.3 Bq m$^{-2}$ h$^{-1}$ to 25.8 Bq m$^{-2}$ h$^{-1}$, and decreased along the length of the transect from around 130 m onwards, probably due to the higher soil moisture content (Figure 5.1b). The coefficient of variation was 55%. The $\text{N}_2\text{O}$ flux was highly variable along the length of the transect (C.V. = 161%), as expected, and showed no trend. Fluxes ranged from 0.61 to 77.0 g $\text{N}_2\text{O}$ N ha$^{-1}$ d$^{-1}$, but were mostly in the range 0.6 to 10 g $\text{N}_2\text{O}$ N ha$^{-1}$ d$^{-1}$. The median $\text{N}_2\text{O}$ flux was 3.6 g $\text{N}_2\text{O}$ N ha$^{-1}$ d$^{-1}$. No significant correlation was found between the log-transformed $\text{N}_2\text{O}$ fluxes and any of the variables measured. $^{222}\text{Rn}$ flux was most strongly correlated with soil moisture ($r = -0.48$, p < 0.01), but the coefficient of determination was only ~ 20%. For data > 130 m from the start of the transect only, $r^2$ was the same. $^{222}\text{Rn}$ flux was also found to correlated with soil temperature ($r = -0.39$ and $r = -0.32$ for soil surface and 10 cm-depth temperatures, respectively), but these correlations are in the wrong direction to suggest the importance of any temperature-controlled physical processes which affect $^{222}\text{Rn}$ flux. No significant
correlation was found between the log-transformed N₂O fluxes and any of the variables measured.

Figure 5.2. ²²²Rn fluxes (a), soil moisture content (b), and N₂O fluxes (c) measured at 4 m intervals along a 200 m transect.
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Spatial studies of $^{222}$Rn flux

Table 5.3. Summary statistics for the transect study.

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs.</th>
<th>Mean</th>
<th>Median</th>
<th>Std. dev.</th>
<th>Min</th>
<th>Max</th>
<th>Skewness</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>50</td>
<td>11.2</td>
<td>10.5</td>
<td>6.1</td>
<td>1.3</td>
<td>25.8</td>
<td>0.42</td>
<td>55</td>
</tr>
<tr>
<td>N$_2$O flux (g N$_2$O-N ha$^{-1}$ d$^{-1}$)</td>
<td>50</td>
<td>7.5</td>
<td>3.6</td>
<td>12.0</td>
<td>0.61</td>
<td>76.78</td>
<td>4.39</td>
<td>161</td>
</tr>
<tr>
<td>Soil moisture (m$^3$ m$^{-3}$)</td>
<td>50</td>
<td>0.56</td>
<td>0.55</td>
<td>0.04</td>
<td>0.45</td>
<td>0.65</td>
<td>0.29</td>
<td>8</td>
</tr>
<tr>
<td>Soil surface temperature (°C)</td>
<td>50</td>
<td>3.5</td>
<td>3.5</td>
<td>0.5</td>
<td>2.0</td>
<td>4.6</td>
<td>-0.56</td>
<td>13</td>
</tr>
<tr>
<td>Soil temperature at 10 cm (°C)</td>
<td>50</td>
<td>2.7</td>
<td>2.7</td>
<td>0.6</td>
<td>1.1</td>
<td>3.7</td>
<td>-0.41</td>
<td>21</td>
</tr>
</tbody>
</table>

*Skewness after log$_{10}$-transformation was 0.66.

The variograms for $^{222}$Rn flux, N$_2$O flux, and soil moisture content are shown in Figure 5.3. The semivariances were computed from the raw $^{222}$Rn flux and soil moisture data, and the log$_{10}$ transformed N$_2$O flux data, using Equation (5.1). The data were checked for the observed trends (Figure 5.2) by fitting linear and quadratic lines on the coordinates, but none were found to be significant enough to warrant computing the variogram on the residuals (about 21% for $^{222}$Rn flux and soil moisture content, but virtually none for N$_2$O flux). The $^{222}$Rn flux variogram indicates spatial dependence in $^{222}$Rn fluxes above ~ 40 m (indicated by the monotonically increasing part of the plot), but below this level fluxes were spatially uncorrelated (nugget variance). The lack of sill indicates that the transect had not covered the full range of spatial dependence, as would be expected for such a short transect. The soil moisture content also indicates spatial dependency above ~ 40 m. At first site, the N$_2$O flux variogram indicates nugget variance only, however, it is also possible that there may have been a periodicity of wavelength of ~ 15-18 m.
Figure 5.3. Variograms for: (a) $^{222}$Rn flux, (b) soil moisture, and (c) N$_2$O flux.
5.3.2 Regional-scale variability

Mean $^{222}\text{Rn}$ fluxes, gamma dose rates, $^{226}\text{Ra}$ activities of the soil, and other soil properties measured at each site are given in Table 5.4, and summary statistics for each variable are given in Table 5.5. Mean $^{222}\text{Rn}$ fluxes followed an approximately log-normal distribution (Figure 5.4), and ranged from 0.8 Bq m$^{-2}$ h$^{-1}$ (measured at Ulsta, site 9) to 236 Bq m$^{-2}$ h$^{-1}$ (measured at Muckle Roe, site 15). The median $^{222}\text{Rn}$ flux was 9.7 Bq$^{-2}$ h$^{-1}$, and the quartile deviation 7.9 Bq$^{-2}$ h$^{-1}$. The coefficient of variation was 204%. The peat soils (sites 3 and 9) and those developed on basic igneous rocks (sites 6 and 8) had the smallest mean fluxes (0.2-1.5 Bq m$^{-2}$ h$^{-1}$), and those developed on granite bedrock (sites 11 and 13) had the largest fluxes (104-236 Bq m$^{-2}$ h$^{-1}$). The largest $^{222}\text{Rn}$ flux recorded was 335 Bq m$^{-2}$ h$^{-1}$, measured at Muckle Roe (site 13).

The $^{226}\text{Ra}$ content of the soil was near-normally distributed (Table 5.5), and ranged from < 3 Bq kg$^{-1}$ to 55 Bq kg$^{-1}$ (Table 5.4). The mean flux was ~20 Bq kg$^{-1}$, which is lower than the world average of 35 Bq kg$^{-1}$ (UNSCEAR, 2000). In relation to the parent material, the $^{226}\text{Ra}$ content of the soil generally followed the distribution that would be expected, with the highest $^{226}\text{Ra}$ activities for soils developed on bedrock rich in uranium (granites – sites 1 and 13), and the lowest activities for soils developed on material with a low uranium content (basic igneous rocks – sites 6 and 8) (Tables 5.1 and 5.4).

Gamma dose rates were log-normally distributed. Mean gamma dose rates ranged from 14 nGy h$^{-1}$ to 45 nGy h$^{-1}$, and followed a similar pattern to the $^{222}\text{Rn}$ fluxes, with the smallest dose rates recorded at Ulsta (site 9), and the largest at Noss Hill (site 11), which had the second largest mean $^{222}\text{Rn}$ flux (Table 5.4). Gamma dose rate was not as variable as $^{222}\text{Rn}$ flux however, with a coefficient of variation of 77% (Table 5.5).
Table 5.4. Mean $^{222}\text{Rn}$ fluxes, gamma dose rates and soil properties at 15 sites in North Britain.

<table>
<thead>
<tr>
<th>Site</th>
<th>222Rn flux (Bq m$^{-2}$ h$^{-1}$)</th>
<th>Gamma dose rate (nGy h$^{-1}$)</th>
<th>Ra-226 activity$^a$ (Bq kg$^{-1}$)</th>
<th>Particle size fractions (%)</th>
<th>Texture class (FAO)</th>
<th>Soil depth (m)</th>
<th>Water depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std. dev.</td>
<td>Min.</td>
<td>Max.</td>
<td>No. of obs.</td>
<td>Mean</td>
<td>Min.</td>
</tr>
<tr>
<td>Botany Garden$^b$ (1)</td>
<td>35.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flotterstone (2)</td>
<td>17.2</td>
<td>13.7</td>
<td>3.7</td>
<td>51.3</td>
<td>16</td>
<td>0</td>
<td>27 ± 9</td>
</tr>
<tr>
<td>Harwood (3)</td>
<td>1.0</td>
<td>0.9</td>
<td>0.2</td>
<td>2.7</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Griffin (4)</td>
<td>9.7</td>
<td>4.1</td>
<td>2.7</td>
<td>16.0</td>
<td>11</td>
<td>0</td>
<td>25$^c$</td>
</tr>
<tr>
<td>Scatness (5)</td>
<td>14.9</td>
<td>5.2</td>
<td>10.3</td>
<td>20.9</td>
<td>4</td>
<td>34.2</td>
<td>33.9</td>
</tr>
<tr>
<td>Baltasound (6)</td>
<td>1.5</td>
<td>2.4</td>
<td>-1.0</td>
<td>3.9</td>
<td>3</td>
<td>13.8</td>
<td>13.5</td>
</tr>
<tr>
<td>Belmont (7)</td>
<td>12.5</td>
<td>9.9</td>
<td>6.4</td>
<td>23.8</td>
<td>3</td>
<td>9.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Baltasound RS (8)</td>
<td>0.8</td>
<td>-</td>
<td>0.6</td>
<td>1.0</td>
<td>2</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Ulsta (9)</td>
<td>0.2</td>
<td>0.6</td>
<td>-1.0</td>
<td>1.5</td>
<td>4</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>West Yell (10)</td>
<td>11.8</td>
<td>7.6</td>
<td>3.6</td>
<td>18.7</td>
<td>3</td>
<td>19.3</td>
<td>18.3</td>
</tr>
<tr>
<td>Noss Hill (11)</td>
<td>104</td>
<td>-</td>
<td>86.5</td>
<td>121</td>
<td>2</td>
<td>78.3</td>
<td>77.9</td>
</tr>
<tr>
<td>Eshaness (12)</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>48.4</td>
<td>48.1</td>
</tr>
<tr>
<td>Muckle Roe (13)</td>
<td>236</td>
<td>-</td>
<td>137.0</td>
<td>335</td>
<td>2</td>
<td>56.8</td>
<td>56.8</td>
</tr>
<tr>
<td>Virkie (14)</td>
<td>6.4</td>
<td>-</td>
<td>3.8</td>
<td>9.1</td>
<td>2</td>
<td>27.2</td>
<td>26.6</td>
</tr>
<tr>
<td>Fetlar (15)</td>
<td>2.1</td>
<td>-</td>
<td>1.5</td>
<td>2.7</td>
<td>2</td>
<td>14.2</td>
<td>13.9</td>
</tr>
</tbody>
</table>

$^a$Ra-226 activities are equivalent activities determined from the mean of the $^{210}\text{Pb}$ (295 keV), $^{214}\text{Pb}$ (352 keV) and $^{214}\text{Bi}$ (609 keV) activities. $^b$Data are means of the two locations of measurement (Chapter 4). $^c$The Ra content is a weighted average calculated from the depths of the organic (0.12 m) and mineral (0.88 m) layers and assuming a negligible $^{226}\text{Ra}$ content of the organic layer. $^d$Peat; no textural classification.
Table 5.5. Summary statistics for the regional study.

<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of obs.</th>
<th>Std. Mean</th>
<th>Quart. Mean</th>
<th>Quart. Median</th>
<th>Min.</th>
<th>Max.</th>
<th>Skewness</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}\text{Rn}$ flux (Bq m$^{-2}$ h$^{-1}$)</td>
<td>15</td>
<td>30.6</td>
<td>62.4</td>
<td>9.7</td>
<td>7.9</td>
<td>0.2</td>
<td>235.7</td>
<td>2.99</td>
</tr>
<tr>
<td>Gamma dose rate (nGy h$^{-1}$)</td>
<td>10</td>
<td>30.8</td>
<td>23.6</td>
<td>23.3</td>
<td>18.9</td>
<td>6.2</td>
<td>78.3</td>
<td>0.99</td>
</tr>
<tr>
<td>$^{226}\text{Ra}$ activity (Bq kg$^{-1}$)</td>
<td>15</td>
<td>19.1</td>
<td>17.1</td>
<td>13.0</td>
<td>14.8</td>
<td>0.0</td>
<td>55.0</td>
<td>0.69</td>
</tr>
<tr>
<td>Soil depth (m)</td>
<td>15</td>
<td>0.48</td>
<td>0.51</td>
<td>0.22</td>
<td>0.40</td>
<td>0.08</td>
<td>1.70</td>
<td>1.28</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>13</td>
<td>2.3</td>
<td>1.6</td>
<td>1.9</td>
<td>0.7</td>
<td>0.4</td>
<td>5.7</td>
<td>1.29</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>13</td>
<td>23.8</td>
<td>10.1</td>
<td>25.3</td>
<td>8.3</td>
<td>6.3</td>
<td>38.5</td>
<td>-0.24</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>13</td>
<td>73.9</td>
<td>11.1</td>
<td>73.1</td>
<td>10.6</td>
<td>59.6</td>
<td>93.3</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Figure 5.4. Log-normal cumulative probability distribution for $^{222}\text{Rn}$ flux with 95% confidence intervals.
Mean $^{222}$Rn fluxes for each site were strongly correlated with the $^{226}$Ra activity of the soil (Figure 5.5) and the mean gamma dose rate (Figure 5.6), but no significant correlation was found with any other variables.

**Figure 5.5.** Correlation between mean $^{222}$Rn flux and mean $^{226}$Ra activity of the soil.

**Figure 5.6.** Correlation between mean $^{222}$Rn flux and mean gamma dose rate.
Regression analysis gave the following relationship for $^{222}$Rn flux and gamma dose rate:

$$J_{Rn-222} = 0.00764 \xi^{2.2}$$

(5.2)

where $J_{Rn-222}$ is the radon flux in units Bq m$^{-2}$ h$^{-1}$ and $\xi$ is the gamma dose rate in units nGy h$^{-1}$. Figure 5.7 shows all gamma dose rates and concurrently measured $^{222}$Rn fluxes (n = 12). The correlation coefficient was $r = 0.63$ (p<0.05).

Figure 5.7. Gamma dose rates and $^{222}$Rn fluxes measured in parallel. Gamma dose rates are the average of two measurements: one made at the start of the $^{222}$Rn flux measurement, and one at the end. The numbers in brackets indicate the number of measurement at that site, when more than one parallel measurement was carried out at a particular site. The $^{222}$Rn flux from the peat at Ulsta was <0.01 Bq m$^{-2}$ h$^{-1}$ on this occasion.

5.3.3 Global-scale variability

Figure 5.8 shows $^{222}$Rn fluxes and the percentage of land mass covered by wetlands plotted against latitude, for the Northern Hemisphere. $^{222}$Rn flux data for the Southern
Figure 5.8. $^{222}\text{Rn}$ fluxes and the percentage landmass covered by wetlands in the Northern Hemisphere. (a) Directly-measured $^{222}\text{Rn}$ fluxes (chamber measurements); (b) indirect $^{222}\text{Rn}$ flux estimates derived from atmospheric profile measurements; and (c) wetlands as a percentage of total land area. Directly measured $^{222}\text{Rn}$ fluxes are mean values for a number of studies reported in Turekian et al., (1977) and Conen and Robertson (2002) [Table 1, Appendix A], and indirect $^{222}\text{Rn}$ fluxes are values reported in Turekian et al., (1977). Wetlands data are from Stillwell-Soller et al., (1995).
Hemisphere are limited, and showed no trend with latitude or longitude (data not shown). Directly measured $^{222}$Rn fluxes (chamber measurements) showed a large scatter with latitude, as expected, but indirect flux estimates made from atmospheric profiles showed a clear trend of a decreasing $^{222}$Rn flux with increasing latitude, decreasing from $\sim 1$ atom cm$^{-2}$ s$^{-1}$ (76 Bq m$^{-2}$ h$^{-1}$) at 30°N to $\sim 0.2$ atom cm$^{-2}$ s$^{-1}$ (15 Bq m$^{-2}$ h$^{-1}$) at 70°N. $^{222}$Rn flux estimates derived from $^{210}$Pb fluxes (Conen and Robertson, 2002/Appendix A), and recent flux estimates derived from atmospheric profile data measured at a tall tower in Eastern Siberia, also support this trend (J. Moriizumi, pers. comm.).

5.4 Discussion

5.4.1 Spatial variability of $^{222}$Rn flux

Local scale variability

The transect study showed that $^{222}$Rn emissions were approximately log-normally distributed on (as opposed to the log-normal distribution found on the regional scale), and much less variable than N$_2$O emissions (CVs were 55% and 161% for $^{222}$Rn flux and N$_2$O flux respectively). This comparison illustrates the value of using $^{222}$Rn as a tracer of N$_2$O emissions, as, given the observed variability, many more flux measurements are required to achieve a specified standard error for N$_2$O than for $^{222}$Rn (in this case, approximately 250 samples for N$_2$O, and 25 for $^{222}$Rn for an error of $\sim 10\%$). Soil moisture appeared to be a factor influencing $^{222}$Rn flux (Fig. 4.2), but it could only account for $\sim 20\%$ (r = -0.48) of the observed variability, suggesting that other factors, such as variations in the compactness of the soil, were more important. If the water content of the soil could have been expressed as a fraction of the available pore space (i.e. taking into account variations in the porosity of the soil), it is most likely that a larger proportion of the variability could be explained. Given that the study was carried out on one soil type only, variations in soil texture are unlikely to be a major factor.
The level spatial variability in $N_2O$ fluxes observed (more than two orders of magnitude) was typical for a grazed grassland on this scale (Veltholf et al., 1996; Dobbie et al., 1999). $N_2O$ emissions are highly variable from grazed fields, as an uneven distribution of animal excreta leads to localised and heterogeneously distributed high concentrations of mineralisable N in grassland soil, and thus highly spatially variable 'hot spots' of denitrification and $N_2O$ fluxes. Comparing the coefficients of variation for the two gases (Tables 5.2 and 5.3), it can be seen that a much smaller number of samples would be needed to obtain a desired level of precision for $^{222}Rn$ than for $N_2O$. Hence, as estimates of $N_2O$ emissions are generally chamber-based due to the very small concentrations which require detection, it may be possible to obtain more accurate emissions estimates of $N_2O$ by using $^{222}Rn$ as a tracer (Conen et al., 2002).

**Regional-scale variability**

The mean $^{222}Rn$ fluxes recorded at 15 sites of differing soil type and geology show that the $^{222}Rn$ emissions from North Britain are highly variable, as expected, with fluxes ranging from $< 1$ Bq m$^{-2}$ h$^{-1}$ to $\sim 230$ Bq m$^{-2}$ h$^{-1}$. As expected, the peat (Ulsta and Harwood) and those developed on basic igneous rocks (Baltasound RS and Baltasound) had the lowest $^{226}Ra$ contents ($< 3$ Bq kg$^{-1}$ for the igneous soils, and assumed to be negligible for peat) had the smallest mean fluxes, and the soils developed on granite (Noss Hill and Muckle Roe) had the highest $^{226}Ra$ contents ($> 45$ Bq kg$^{-1}$) and largest mean fluxes. The $^{226}Ra$ content for the soil was found to account for a large proportion of the variability in mean $^{222}Rn$ fluxes (~80%), but, apart from gamma dose rate, $^{222}Rn$ flux was not found to correlate with any other variable. However, as these measurements were made on medium and coarse-textured soils only, and mostly on very shallow soils ($< 0.3$ m), the variability in $^{222}Rn$ emissions due to these latter factors is masked by the large variability due to variations in the $^{226}Ra$ content of the soil. In their survey of $^{222}Rn$ emissions from Australian soils, Schery et al. (1989) found only a modest correlation between $^{222}Rn$ flux and soil $^{226}Ra$ content, and concluded that spatial
variations in the emanating fraction were responsible for most of the variability (and thus that variations in soil texture were important). Thus, the large proportion of variability explained by $^{226}$Ra content alone in the present study is at least partly due to the fact that the study sites did not encompass the full range of soil texture variations, but it is probably also because the data used in this study are site means, rather than spot measurements.

The median flux of 9.7 Bq m$^{-2}$ h$^{-1}$ is much lower than estimates of the global average, which range from ~50 Bq m$^{-2}$ h$^{-1}$ to ~100 Bq m$^{-2}$ h$^{-1}$ (Lambert et al., 1982; Wilkening et al., 1975). Given the relatively large proportion of peat and peaty podzol soils, and generally higher soil moisture content and water tables for the region, a much lower than average $^{222}$Rn flux would be expected for North Britain; however, as most of the measurements were carried out on shallow and peaty soils, it is likely that this value is lower than the actual mean flux from North Britain.

Global scale variability

The indirect flux measurements support the hypothesis of a decreasing flux with increasing latitude due to the greater proportion of wetlands at high latitudes. However, this factor can only explain part of the trend, as the $^{222}$Rn flux decreases by ~80% between 30°N and 70°N, whereas the percentage coverage of wetlands increases from zero to only 14%. Besides the increase in wetlands, increased snow and ice cover at higher latitudes will also be a cause of this trend, and regional gradients in soil $^{226}$Ra content may also be important for some areas, for example, in China the concentration of $^{238}$U decreases from south to north (Xu et al., 1993; Sun et al., 2004). Although it is unlikely that this latitudinal trend in $^{222}$Rn emissions would be observed at any one longitude, given that a spatially homogenous $^{222}$Rn emission rate of 1 atom cm$^{-2}$ s$^{-1}$ (76 Bq m$^{-2}$ h$^{-1}$) from ice-free land surfaces is generally assumed in model validation.
studies it is possible that this trend could prove useful in improving global $^{222}\text{Rn}$ source terms (Chapter 7).

5.4.2 Estimating $^{222}\text{Rn}$ flux using gamma dose rate as a surrogate
The relationship found between $^{222}\text{Rn}$ flux and gamma dose rate (Figure 5.6) was similar to that found by Schery et al., (1989) and Nielson et al., (1996). Schery et al., (1989) found a correlation of $r = 0.62$ for a total of 76 parallel measurements of $^{222}\text{Rn}$ flux and gamma dose rate made on a wide range of soils in Australia, whilst Nielson et al., (1995) found a correlation of $r = 0.53$ for 1020 measurements carried out over the range of soils in Florida, USA. For this research the correlation coefficient for all measurements ($n = 12$) was $r = 0.67$, and for mean $^{222}\text{Rn}$ fluxes and gamma dose rates ($n = 10$) it was $r = 0.87$. The stronger correlation found for the mean values reflects the averaging of temporal variations in the gamma dose rate over time, which are mainly due to variations in the concentration of gamma-emitting radon decay products (Figs 1.1 and 1.2). Atmospheric concentrations of radon and its decay products are largely controlled by atmospheric mixing (e.g. Kataoka et al., 2003), and rainfall, which scavenge aerosols (to which radon daughters quickly become irreversibly attached) from the atmosphere, can cause a significant temporary increase in gamma dose rate (Nishikawa et al., 1995; Yamanishi and Miyake, 2003).

Figure 5.9 shows the mean $^{222}\text{Rn}$ fluxes recorded at the 10 sites where gamma dose rate measurements were made compared to $^{222}\text{Rn}$ fluxes calculated using (a) Eq. (5.2), (b) the function given in Nielson et al., (1996), and (c) a function derived from the data in Schery et al., (1989). The function derived from the present study gives the best overall fit to observations, as would be expected, but the Schery and Nielson functions also gave adequate matches at a number of sites. Neither the Schery or Nielson functions could predict the lower values particularly well, however, suggesting that the data from which
these functions were derived may not have included many measurements from soils which had as low a $^{222}$Rn flux or gamma dose rate as those from which measurements were made in this study.

Conen (2004) has recently illustrated the potential of using routine gamma radiation measurements made by national radiation protection agencies and nuclear power plant operators to provide a spatially-resolved $^{222}$Rn source term. Taking Germany as an example, where gamma radiation is continuously monitored at 2150 stations, predictions showed $^{222}$Rn emissions to be lower in the northern part of the country, and some higher fluxes in the mountainous areas, which matches with the general pattern in $^{222}$Rn soil gas concentrations and radon concentrations measured indoors (Kemski et al., 2001).
Hence, it would seem that this simple relationship clearly has potential for providing a crude description of the spatial distribution in $^{222}$Rn emissions. Given that gamma dose rate is routinely monitored across large parts of the world, these measurements could be used to provide a cheap and quick method of providing regional-scale spatial descriptions of $^{222}$Rn emissions, especially for regions where the monitoring network is quite dense. However, considering the slightly stronger correlation between the $^{222}$Rn flux and the $^{226}$Ra content of the soil ($r = 0.91$, Fig. 5.5) compared to that between $^{222}$Rn flux and gamma dose rate ($r = 0.87$, Fig. 5.6), it is also possible that, where this data was available, the $^{226}$Ra content of the soil could prove to be an as good, or even better, predictor of $^{222}$Rn emissions. Conen (2004) has also investigated using gamma dose rate to predict the temporal variation in $^{222}$Rn flux; however, although the gamma dose rate is somewhat attenuated by higher soil moistures (Peck et al., 1992), the effect is not as large as for $^{222}$Rn flux, and temporal variations in atmospheric concentrations of radon and its decay products (and thus the gamma dose rate) are largely controlled by atmospheric mixing (Kataoka et al., 2003), rather than changes in the radon flux. Thus, it seems unlikely that it would be possible to adequately estimate the temporal variation in $^{222}$Rn emissions on the basis of the temporal signal in gamma dose rate.

5.5 Summary and conclusions

- $^{222}$Rn emissions were found to be normally distributed on the local scale, and much less variable than biogenically-produced N$_2$O. On the regional scale $^{222}$Rn emissions were approximately log-normally distributed, and correlated strongly with the $^{226}$Ra content of the soil. Mean $^{222}$Rn fluxes were also found to be strongly correlated with the mean gamma dose rate.

- $^{222}$Rn emissions from North Britain are highly variable because of the complex geology of this region, and thus the wide range in soil $^{226}$Ra content. The average flux from North Britain is likely to be substantially less than global average values,
due to the relatively large proportion of peat and peaty podzol soils, and generally higher soil moisture contents and water tables.

- On the global scale there is a general decrease in $^{222}$Rn flux with increasing latitude in the Northern Hemisphere which is most likely caused by the greater proportion of wetlands at higher latitudes. This trend could prove useful in improving global $^{222}$Rn source terms used in models.

- Surveys of the $^{226}$Ra content of the soil and routine gamma radiation measurements made by national radiation protection agencies and nuclear power plant operators, could be used to provide a cheap and relatively fast method of providing descriptions of the spatial distribution of $^{222}$Rn emissions for large parts of the world.
Chapter 6

A $^{222}\text{Rn}$ emissions map of North Britain based on soil type and bedrock geochemistry

6.1 Introduction

$^{222}\text{Rn}$ flux measurements made at 15 sites of different soil type and bedrock in North Britain indicate that emissions from this region are highly variable, with fluxes ranging from $< 1 \text{ Bq m}^{-2} \text{ h}^{-1}$ to $> 200 \text{ Bq m}^{-2} \text{ h}^{-1}$ (Chapter 5). In atmospheric studies using $^{222}\text{Rn}$ as a tracer, such as estimating the magnitude of trace gas fluxes (e.g. Kuhlmann et al., 1998; Levin et al., 1999) or validations of mesoscale atmospheric transport models (Chevillard et al., 2002), it would be desirable to take this variability into account. For this purpose, a $^{222}\text{Rn}$ emissions map of North Britain has been produced. The map was created using a GIS, taking a similar approach to that of Eckhardt (1990), who produced a $^{222}\text{Rn}$ emissions map for Europe using the Food and Agriculture Organisation (FAO) digital soil map of the world (FAO, 1995) and $^{222}\text{Rn}$ flux data for soils around Europe. In the present map, British Geology Survey (BGS) solid geology data have also been used, as a surrogate for the geographical variation in the $^{226}\text{Ra}$ content of the soil. The map is compared to the BGS $^{222}\text{Rn potential}$ map of the same region (Appleton and Ball, 1995), and national maps of the gamma dose rate and indoor $^{222}\text{Rn}$ concentrations (Green, 1992; NRPB, 2000). Limitations and sources of error with the map are discussed.
6.2 Materials and Method

6.2.1 Materials

The map was produced using the ARC/Info GIS program, the FAO Digital Soil Map of the World (FAO, 1995), digital solid geology data licensed from the BGS, and information on \( ^{222}\text{Rn} \) emissions from different soil types derived from field measurements (Chapter 5) and values reported in the literature\(^1\). The FAO Digital Soil Map of the World is based on the FAO/UNESCO Soil Map of the World, original scale 1:5,000,000. The CD-ROM contains two types of files: map sheets and derived soil properties files. The latter include information on a number of attributes such as soil texture, depth, pH, organic matter content, slope and drainage class. The cell size of the raster data is 5 x 5 arc-minutes (equivalent to 3 km x 3 km at the equator). Much more detailed soils data than this are available for Scotland in the form of maps held by the Macaulay Institute, Aberdeen, and for England and Wales maps produced by the National Soil Resources Institute, Cranfield University (Silsoe, Bedfordshire); however, due to the financial constraints of this project it was not possible to use these data. The geology data used were licensed in the form of attributed vector data at a 250 m x 250 m resolution.

6.2.2 Method

\( ^{222}\text{Rn} \) emissions were modelled using the following equation:

\[
J_{\text{Rn-222}} = J_A R T
\]

(6.1)

where \( J_A \) is a mean \( ^{222}\text{Rn} \) flux assigned to each soil type, \( R \) is a scaling factor to take into account variations in the \( ^{226}\text{Ra} \) content of the soil, and \( T \) is a scaling factor to take into account variations in the

---

\(^1\) Production of the map was carried out by L. Spedavecchia, under the supervision of Dr J. Wright, as part of his 4\(^{th}\) year BSc GIS module.
account variations in the texture of the soil. Thus, building the empirical $^{222}$Rn emissions model involved three steps:

1) assigning a mean $^{222}$Rn flux to each FAO soil type (for an average soil $^{226}$Ra content and medium texture);
2) accounting for variations in the $^{226}$Ra content of the soil;
3) accounting for variations in soil texture.

Assigning a mean $^{222}$Rn flux to the FAO soil types

A $^{222}$Rn flux value was assigned to each FAO soil classification present in the region of interest (defined by the BGS North Britain 1:650,000 solid geology map) on the basis of:
a) field measurements i.e. using the mean $^{222}$Rn flux for that soil type based on the measurements reported in Chapter 5; or b) a value based on mean $^{222}$Rn fluxes reported in the literature; or c) the same value as another soil classification, on the basis of their similarity to that soil in terms of properties such as organic matter content and typical water table depth/drainage characteristics. Table 6.1 shows the $^{222}$Rn fluxes assigned to each soil type, for an average $^{226}$Ra content of 25-35 Bq kg$^{-1}$ (based on the results reported in Chapter 5) and medium soil texture. Where a $^{222}$Rn flux value was not available for the average $^{226}$Ra content range for a particular soil type, a value was estimated using the function:

$$J_{Rn-222} = 1.6 e^{0.1A_{Ra-226}}$$

(6.2)

where $A_{Ra-226}$ is the $^{226}$Ra activity of the soil (Chapter 5, Figure 5.5).
Chapter 6  

Table 6.1. $^{222}$Rn fluxes assigned to each FAO soil type, for an average soil $^{226}$Ra content of 25-35 Bq kg$^{-1}$ and a medium soil texture.

<table>
<thead>
<tr>
<th>FAO Soil Type</th>
<th>$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)</th>
<th>Method</th>
<th>Texture scaling</th>
<th>Geology scaling</th>
<th>Area covered (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gleysols</td>
<td>14.5</td>
<td>Field measurements</td>
<td>Yes</td>
<td>Yes</td>
<td>33.4</td>
</tr>
<tr>
<td>Cambisols</td>
<td>35</td>
<td>Field measurements</td>
<td>Yes</td>
<td>Yes</td>
<td>25.5</td>
</tr>
<tr>
<td>Podzols</td>
<td>10</td>
<td>Field measurements</td>
<td>Yes</td>
<td>Yes</td>
<td>17.6</td>
</tr>
<tr>
<td>Histosols</td>
<td>0.6</td>
<td>Field measurements</td>
<td>No</td>
<td>No</td>
<td>11.0</td>
</tr>
<tr>
<td>Luvisols</td>
<td>14.5</td>
<td>Assumed same as Gleysols</td>
<td>Yes</td>
<td>Yes</td>
<td>4.6</td>
</tr>
<tr>
<td>Rankers</td>
<td>42</td>
<td>Estimated</td>
<td>No</td>
<td>Yes</td>
<td>4.0</td>
</tr>
<tr>
<td>Lithosols</td>
<td>7.5</td>
<td>Estimated</td>
<td>No</td>
<td>Yes</td>
<td>1.1</td>
</tr>
<tr>
<td>Arenosols</td>
<td>50</td>
<td>Assumed same as Regosols</td>
<td>No</td>
<td>Yes</td>
<td>1.1</td>
</tr>
<tr>
<td>Rendzinas</td>
<td>22</td>
<td>Estimated</td>
<td>Yes</td>
<td>No</td>
<td>1.1</td>
</tr>
<tr>
<td>Regosols</td>
<td>50</td>
<td>Field measurements</td>
<td>No</td>
<td>Yes</td>
<td>0.4</td>
</tr>
<tr>
<td>Podzoluvisols</td>
<td>14.5</td>
<td>Assumed same as Podzols</td>
<td>Yes</td>
<td>Yes</td>
<td>0.2</td>
</tr>
</tbody>
</table>

$^{222}$Rn flux value based on field measurements (for an average $^{226}$Ra content and medium soil texture) was available for: Cambisols (the Botany Garden site average); Gleysols (the average of the Flotterstone and West Yell sites); Podzols (Griffen); Regosols (Virkie); and Histosols (the average of the Harwood and Ulsta sites). On the basis of their similarity, Luvisols were assigned the same $^{222}$Rn flux as Gleysols, Podzoluvisols the same as Podzols, and Arenosols the same as Regosols. Values for Lithosols and Rankers were extrapolated (using Eq. 6.2) from mean fluxes reported in Wilkening (1974) and Whittlestone et al. (1996), respectively. Rendzinas, which exclusively form on limestones, were also assigned a $^{222}$Rn flux extrapolated from the data in Whittlestone et al. (1996).
Adjusting emissions for variations in the soil $^{226}$Ra content

As the composition of mineral soils is strongly determined by the parent material (Rawlins et al., 2003; Goovaerts and Webster, 1994), geology maps can be useful for estimating the geochemical content of soils (Rawlins et al., 2003). In this study, only the bedrock geology has been used to estimate the $^{226}$Ra content of the soil. In a study carried out to investigate the relative importance of parent material as a factor influencing topsoil geochemistry, Rawlins et al. (2003) found that a classification by parent material (i.e. taking into account the unconsolidated sediments) accounted for more of the variance of the $^{238}$U content of the soil (and many other elements) than a classification based on the solid geology alone. However, as the $^{226}$Ra content of the Quaternary sediments is largely unknown, and it is difficult to make useful generalisations, this information has not been included in the map. Nevertheless, numerous studies have shown that the $^{226}$Ra content of the soil is strongly related to bedrock geology (Wollenberg and Revzan, 1990; Duval and Otton, 1990; Gates and Gunderson, 1992; McAulay and Marsh, 1992; Anagnostakis et al., 1996; O’Dea and Dowdall, 1999; Ielsch et al., 2002).

For each lithology (a total of 96), an average $^{238}$U or $^{226}$Ra soil content (Bq kg$^{-1}$) was calculated on the basis of average values reported for different rock types in the literature (Wiegand, 2001; Tyler, 1994; Ielsch et al., 2001; Quindos et al., 2003; Qureshi et al., 2001; Singh et al., 2003). $^{222}$Rn emissions scaling factors were then calculated for 8 different $^{238}$U/$^{226}$Ra contents (Table 6.2), using a $^{222}$Rn flux calculated for each average $^{238}$U/$^{226}$Ra soil content, using Eq. 6.2. Secular equilibrium between $^{226}$Ra and $^{238}$U was assumed. These scaling factors were applied to all soil types except Histosols (Table 6.1), to which they are not applicable as they are organic soils. Examples of rock types in the different scaling factor groupings are given in Table 6.2.
Table 6.2 Scaling factors for the $^{226}$Ra content of the soil based on the $^{238}$U content of the bedrock.

<table>
<thead>
<tr>
<th>$^{238}$U content range (ppm)</th>
<th>Scaling factor</th>
<th>Examples of rock types</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.5</td>
<td>0.1</td>
<td>Serpentine</td>
</tr>
<tr>
<td>0.5-1</td>
<td>0.2</td>
<td>Basalts, gabbro, eclogites</td>
</tr>
<tr>
<td>1-2</td>
<td>0.3</td>
<td>Sandstones, greywakes, gritstones, phylite</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>Limestone</td>
</tr>
<tr>
<td>2-3</td>
<td>1.0</td>
<td>Andesites, diorites, shales (excluding black), schist, gneiss, mudstones</td>
</tr>
<tr>
<td>3.5-4</td>
<td>3.9</td>
<td>Rhyolites, clays</td>
</tr>
<tr>
<td>4</td>
<td>5.9</td>
<td>Granites</td>
</tr>
<tr>
<td>4-5</td>
<td>9.0</td>
<td>Black shales, granulite</td>
</tr>
</tbody>
</table>

Adjusting emissions for variations in soil texture

Scaling factors of 1.7 for fine soils, and 0.3 for coarse soils, relative to medium-textured soils, were derived from $^{222}$Rn flux measurements reported in Dörr and Münnich (1990), who noted an empirical relation between $^{222}$Rn flux and soil texture. Scaling factors were also calculated from mean values of the emanating fraction measured for soils of different texture by Damkjær and Korsbech (1985); however, the values derived from the flux measurements were considered to be more realistic (scaling factors calculated from mean emanating fractions were 1.1 for fine and 0.5 for coarse soils, respectively). Soil types for which variations in texture were taken into account are indicated in Table 6.1.
6.3 Results and Discussion

6.3.1 $^{222}$Rn emissions map of North Britain

The $^{222}$Rn emissions map of North Britain is shown in Figure 6.1, and for the Shetland Islands only, where a number of $^{222}$Rn flux measurements have been made (Chapter 5), in Figure 6.2. The maps show detail at a resolution of 250 m x 250 m, but because of the resolution of the FAO soils map the working resolution of the map is 3 km x 3 km. Predicted fluxes range from 0 to 221 Bq m$^{-2}$ h$^{-1}$, which is similar to the range of fluxes measured in the field (0 – 236 Bq m$^{-2}$ h$^{-1}$ – Table 5.4, Chapter 5). The median predicted flux is 5 Bq m$^{-2}$ h$^{-1}$, which is somewhat lower than the median $^{222}$Rn flux calculated from mean $^{222}$Rn fluxes at the 15 sites at which measurements were made (9.7 Bq m$^{-2}$ h$^{-1}$ – Table 5.5), and is considerably lower than estimates of the global mean flux, which range from ~ 50 to 100 Bq m$^{-2}$ h$^{-1}$ (Lambert et al., 1982; Wilkening et al., 1975). A lower than average $^{222}$Rn flux would be expected for this region, because of the relatively large proportion of peat soils (11%), which generally have very low $^{222}$Rn emissions due to their low $^{226}$Ra content (Table 5.4), but also because of the generally higher soil moisture content and water tables of soils in this region.

A number of geological features/lithologies can easily be recognized from the pattern in $^{222}$Rn emissions on the map, reflecting the much finer resolution of the geology map compared to the soils map. For example, the Dalbeattie Granite and Cairnsmore of Fleet Granite domes in Dumfries appear as areas of relatively high $^{222}$Rn emissions (Figure 6.3, features A and B). These features are also clearly visible as areas of enhanced radioactivity in aerial gamma-ray spectrometry surveys of this region (Sanderson et al., 2003). The locality with the highest $^{222}$Rn emissions (> 200 Bq m$^{-2}$ h$^{-1}$) – feature C in the centre of the map - corresponds to the presence of Quartz-Feldspar-Granulites, and the elongated feature in Northumberland with emissions in the range 100-200 Bq m$^{-2}$ h$^{-1}$ corresponds to Ampthill and Kimmeridge clays (Figure 6.3, feature D). These lithologies were all assigned the highest $^{238}$U/$^{226}$Ra scaling factor.
Figure 6.1. $^{222}$Rn flux map of North Britain based on the FAO world soils map and BGS 1:650,000 solid geology map (IPR/44-20C British Geological Survey. © NERC. All rights reserved). Sites where $^{222}$Rn flux measurements have been made are indicated by the white dots.
Figure 6.2. $^{222}$Rn flux map of the Shetland Islands, expanded from Figure 6.1 (IPR/44-20C British Geological Survey. © NERC. All rights reserved). Sites where $^{222}$Rn flux measurements have been made are indicated by white dots.
Chapter 6  
A $^{222}$Rn emissions map of North Britain

**$^{222}$Rn flux (Bq m$^{-2}$ h$^{-1}$)**

- **Water**: < 5 - 10
- **< 1**: 5 - 10
- **10 - 20**: 10 - 20
- **20 - 50**: 100 - 200
- **> 200**: > 200

Figure 6.3. Annotated $^{222}$Rn flux map of North Britain (IPR/44-20C British Geological Survey. © NERC. All rights reserved). Sites where $^{222}$Rn flux measurements have been made are indicated by the white dots.
Appleton and Ball (1995) produced a $^{222}\text{Rn}$ potential map for the UK based on solid geology. The north sheet of this map is shown in Figure 6.4. Comparing the radon potential map to the $^{222}\text{Rn}$ flux map, it can be seen that there are some important differences between the maps in terms of indicating areas of enhanced $^{222}\text{Rn}$ emissions. For the far northeast coast of mainland Scotland the BGS map indicates high and very high $^{222}\text{Rn}$ potentials, but the $^{222}\text{Rn}$ flux map predicts $^{222}\text{Rn}$ fluxes in the range 0 to 5 Bq m$^{-2}$ h$^{-1}$ for much of this area (Figure 6.1). This discrepancy is likely to be at least partly due to the prevalence of thick blanket peat over some of this region, from which very low $^{222}\text{Rn}$ emissions were assigned regardless of bedrock type (no $^{226}\text{Ra}$ content scaling was applied to Histosols) (Table 6.1.). The same also applies to much of the Orkney Islands and the western part of Mainland Shetland, where the radon potential map generally indicates a high potential for $^{222}\text{Rn}$ (Fig. 6.4), but predicted $^{222}\text{Rn}$ fluxes are in the range 1 to 5 Bq m$^{-2}$ h$^{-1}$ (Figs. 6.1 and 6.2). A comparison of the two maps with the National Radiological Protection Board (NRPB) maps of indoor radon concentrations (Figure 6.5a) and annual mean outdoor gamma dose rates (Figure 6.5b) indicates that the extreme northeast of Scotland is not an area of enhanced $^{222}\text{Rn}$ flux, except for a small area on the coast (around Helmsdale). This area is indicated as an area of very high $^{222}\text{Rn}$ potential by the BGS map (Figure 6.4). Whilst the $^{222}\text{Rn}$ emissions map does indicate higher emissions for this locality relative to the surrounding area, it is not of a magnitude large enough to match with the NRPB maps. The Dee Valley and Cheviot Hill regions of high radioactivity shown on the NRPB maps (Figs. 6.5a and 6.5b), and indicated by the BGS $^{222}\text{Rn}$ potential map, are not indicated by the $^{222}\text{Rn}$ emissions map particularly well either.
Figure 6.4. BGS Radon potential map of North Britain (Appleton and Ball, 1995; IPR/55-35C1995 British Geological Survey. © NERC. All rights reserved).
Figure 6.5. (a) Mean indoor $^{222}$Rn concentrations measured in homes in the UK (NRPB, 2000); and (b) Outdoor annual mean gamma dose rates for Great Britain (Green, 1992).
6.3.2 Comparison with field measurements

Predicted $^{222}\text{Rn}$ flux values for the cells or polygons where $^{222}\text{Rn}$ flux measurements have been made (Chapter 5) are compared to the observed mean fluxes in Table 6.3 and Figure 6.6. However, as the working resolution of the map (3 km x 3 km) encompasses a range of soil types (i.e. each cell or polygon represents up to four soil types) the predicted fluxes cannot be expected to match particularly well with mean $^{222}\text{Rn}$ fluxes observed for one soil type, so a more general and qualitative comparison is of more value. On the whole, the model underpredicted $^{222}\text{Rn}$ emissions, particularly at the sites with the largest fluxes (Noss Hill and the Botany Garden – Figure 6.6). However, from Figure 6.2 it can be seen that the emissions map predicts higher emissions for the Noss Hill area than for the surrounding region, and, likewise, in line with the observations.

<table>
<thead>
<tr>
<th>Site</th>
<th>Observed</th>
<th>Predicted</th>
<th>Prediction/observation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Botany Garden (1)</td>
<td>35.0</td>
<td>10.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Flotterstone (2)</td>
<td>17.2</td>
<td>10.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Harwood (3)</td>
<td>1.0</td>
<td>6.4</td>
<td>6.7</td>
</tr>
<tr>
<td>Griffen (4)</td>
<td>9.7</td>
<td>3.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Scatness Yard (5)</td>
<td>14.9</td>
<td>1.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Baltasound (6)</td>
<td>1.5</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Belmont (7)</td>
<td>12.5</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>BS Radiostation (8)</td>
<td>0.8</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Ulsta (9)</td>
<td>0.2</td>
<td>5.3</td>
<td>26.3</td>
</tr>
<tr>
<td>West Yell (10)</td>
<td>11.8</td>
<td>5.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Noss Hill (11)</td>
<td>103.8</td>
<td>20.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Eshaness (12)</td>
<td>6.1</td>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Virkie Pool (14)</td>
<td>6.4</td>
<td>9.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*The Fetlar and Muckle Roe sites are not listed as these islands are not included on the FAO soils map.*
Figure 6.6. Predicted and observed mean $^{222}\text{Rn}$ fluxes. Black error bars are the standard deviation, and the grey error bars are the range.
the map also predicts higher fluxes at the Eshaness site than at the Baltasound and Baltasound RS sites. Thus, whilst the map does not reproduce the magnitude of fluxes, it appears to reproduce the main spatial patterns in emissions.

6.3.3 Limitations of the map

Coarse resolution of the soils map

The FAO digital soils map has a resolution of 5 x 5 arc-minutes (equivalent to 3 km x 3 km at the equator), which is factor of 12 greater than the resolution of the geology data. Consequently, each cell or polygon of the soil map does not represent one particular soil type, but up to four (the predicted \(^{222}\text{Rn}\) flux for each polygon is a weighted average \(^{222}\text{Rn}\) flux of that of up to four different FAO soil types). For example, one particular combination of soils for an individual polygon is: 50% Histosols, 20% Podzols, 20% Lithosols, and 10% Gleysols. For an average soil \(^{226}\text{Ra}\) content and medium texture, this combination of soils gives a \(^{222}\text{Rn}\) flux of \(\sim 18\ \text{Bq m}^{-2}\ \text{h}^{-1}\), which is much higher than the value of 0.6 Bq m\(^{-2}\) h\(^{-1}\) assigned to Histosols. Hence, as evident from the comparison of observed and predicted results (Table 6.3; Figure 6.6), the map will tend to significantly over-predict \(^{222}\text{Rn}\) emissions from Histosols where polygons include a significant mineral soil component (e.g. Ulsta, Harwood), and tend to underpredict fluxes from mineral soils where polygons includes a significant Histosol component.

\(^{222}\text{Rn}\) fluxes assigned to each soil type

The field measurements which were used to calculated some of the \(^{222}\text{Rn}\) flux values assigned to the different FAO soil types were made at only a small number of sites (15), and the majority of these flux values were based on only a few spot measurements (Table 5.4). Thus, there is a significant amount of uncertainty in the values used for each soil type, as even for soils of similar \(^{226}\text{Ra}\) content and texture, there will be variations due to other factors, such as soil depth and water table depth. For some soil
types the $^{222}$Rn flux value assigned was a value assumed on the basis of the similarity of that soil type to another for which a value based on measurements was available (Table 6.1). These generalisations may have introduced a significant error in the map. In reality, because of the characteristic subsurface clay layer, $^{222}$Rn emissions from Luvisols and Podzoluvisols may tend to be higher than those from Gleysols (to which they were assigned the same $^{222}$Rn flux). Soils with a higher clay content tend to emit more $^{222}$Rn because of the large surface area of clay particles i.e. higher emanation coefficients (Damkjaer and Korsbech, 1985; Dörr and Münnich, 1990), but also because smaller soil grains tend to be enriched in radionuclides compared to larger grains, because of preferential adsorption onto clay minerals (Megumi and Mamuro, 1977, 1982). Similarly, Regosols were assigned the same $^{222}$Rn flux value as Arenosols, but the former are generally much shallower than Arenosols, and thus would be expected to have lower $^{222}$Rn emissions. The $^{222}$Rn fluxes assigned on the basis of values reported in the literature could also be significantly erroneous. However, given that an average $^{222}$Rn flux based on field measurements was available for those soil types which have the largest area coverage (Table 6.1), these additional sources of error from the minor soil types become less important.

Another source of error relating to the $^{222}$Rn fluxes assigned to each soil type relates to the function used to calculate some of the assigned values (Eq. 6.2). This function was derived from measurements made from soils of a medium and coarse texture only (Chapter 5 - Table 5.2), and therefore probably overestimates $^{222}$Rn fluxes for coarse soils (Regosols, Arenosols, and Rankers), and underestimates for fine soils, because of the relationship between the emanation fraction and size of soil particles (Bossus, 1984; Damkjaer and Korsbech, 1985) (a sharper increase in $^{222}$Rn emissions with increasing $^{226}$Ra content would be expected for medium textured soils than for coarse textured soils). A small effect along these lines is suggested from the data used here (Figure 6.6), however, in this case any difference in $^{222}$Rn emissions between medium and coarse-
textured soils is largely masked by the variability of other factors, such as soil depth, water table depth etc.

Figure 6.6. $^{222}$Rn flux as a function of soil $^{226}$Ra content for medium and coarse soils. Values are from Chapter 5.

Not accounting for variations in soil depth is also likely to be a significant source of error. For example, the $^{222}$Rn flux assigned to Rendzinas is probably too high, as the extrapolated values were based on $^{222}$Rn fluxes from much thicker soils than these. On the other hand, the majority of the $^{222}$Rn flux measurements which have been used as input data were made on fairly shallow soils (< 30 cm), and this would result in a tendency of the map to underestimate emissions from deeper soils. Further, on shallow soils $^{222}$Rn emissions from rocks may also be important. For example, $^{222}$Rn is often a problem in regions with limestone bedrock, because of the relatively high porosity of
these rocks (Appleton and Ball, 1995). Large $^{222}$Rn fluxes may occur in the vicinity of geological faults, due to both enhanced transport and the fact that they are favourable environments for the concentration of mobile elements such as $^{238}$U (Ball et al., 1991).

**Soil $^{226}$Ra content scaling**

As the $^{226}$Ra content of the unconsolidated sediments may be significantly different from the underlying bedrock, estimating the $^{226}$Ra content on the soil on the basis of the average $^{238}$U/$^{226}$Ra content of the bedrock could introduce a significant error in the map. Also, radionuclides may be concentrated in soils relative to their parent material, and this factor of concentration varies for different types of soils. For example, Greeman et al., (1990) found $^{218}$U and $^{232}$Th to be concentrated by a factor of about 10 in soils developed from carbonate bedrock, but by a factor of 1.5-2 for other parent materials (sandstone in particular). The assumption of secular equilibrium between $^{238}$U and $^{226}$Ra is another potential source of error with regard to the $^{226}$Ra scaling factors (the mean $^{226}$Ra content for soil largely being derived from bedrock $^{238}$U data, as opposed to $^{226}$Ra). For example, if preferential leaching of $^{238}$U has taken place, the $^{226}$Ra content can be significantly enhanced relative to the $^{238}$U content. Also, the assumption of a negligible $^{238}$U/$^{226}$Ra content in all organic soil does not always hold true. Depending on the underlying geology and redox condition, organic soils can sometimes have very high concentrations of $^{238}$U (Dowdall and O’Dea, 1999, 2002; O’Dea and Dowdall, 1999).

**Soil texture scaling**

The soil texture scaling factors were derived from a relatively small number of flux measurements within a fairly localised area, and for soils of a medium $^{226}$Ra content only (Dörr and Münnich, 1990). The values used were significantly different to those calculated using data on the mean emanating fraction for soils of different texture by Damkjær and Korsbech (1985). The data shown in Figure 6.6 suggest that for coarse soils a scaling factor closer to the value calculated from mean emanating fractions (0.5)
would have been more realistic. Using a larger scaling factor for coarse soils would also lessen the general under-prediction in $^{222}$Rn emissions by the map.

6.4 Summary and Conclusions

- The $^{222}$Rn emissions map appears to reproduce the main spatial patterns in emissions, but does not reproduce the magnitude of fluxes, and tends to under-predict emissions on the whole.

- The most significant limitations of the map relate to the coarse resolution of the soils data, the limited amount of $^{222}$Rn flux data for input, and a number of assumptions regarding the scaling factors used to account for variations in the $^{226}$Ra content and texture of the soil.
Chapter 7

Test of a northwards-decreasing $^{222}\text{Rn}$ source term by comparison of modelled and observed atmospheric $^{222}\text{Rn}$ concentrations

7.1 Abstract

Model-predicted atmospheric concentrations of $^{222}\text{Rn}$ based on two different $^{222}\text{Rn}$ source terms have been compared to observations in the lower troposphere. One simulation used a globally uniform $^{222}\text{Rn}$ source term from ice-free land surfaces of 1 atom cm$^{-2}$ s$^{-1}$; the other assumed a northwards-decreasing source term (linear decrease from 1 atom cm$^{-2}$ s$^{-1}$ at 30° N to 0.2 atom cm$^{-2}$ s$^{-1}$ at 70° N). Zero emissions were assigned to oceans. The northwards-decreasing source term improved predictions at four out of six stations north of 50° N, reducing the mean prediction/observation ratio from 2.8 to 0.87. In the latitudinal band between 30° N and 50° N, the northwards-decreasing source term resulted in systematic under-prediction of atmospheric $^{222}\text{Rn}$, whereas the uniform source term provided predictions close to observations. Predictions based on the northwards-decreasing source term were significantly ($p<0.01$) better than those based on the uniform source term for an averaged vertical $^{222}\text{Rn}$ profile around 44° N, but were not for one around 38° N. The results indicate that a northwards-decreasing source term

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1 A version of this chapter has been published in *Tellus B*, with D.S. Stevenson (School of GeoSciences, University of Edinburgh) and F. Conen (Environmental Geosciences, University of Basel, Bernoullistrasse 30, 4056 Basel,) as co-authors (Robertson et al., 2005/Appendix B).
could be a more realistic representation of actual $^{222}$Rn emissions than a uniform 1 atom cm$^{-2}$ s$^{-1}$ source term. However, the decrease in $^{222}$Rn source strength with increasing latitude might not begin at 30°N, but somewhat further north. This hypothesis should be investigated through model-independent means.

7.1 Introduction
The radioactive noble gas radon-222 (half-life = 3.82 days) is frequently used in the evaluation and intercomparison of atmospheric transport models (Brost and Chatfield, 1989; Feichter and Crutzen, 1990; Genthon and Armengaud, 1995; Lin et al., 1996; Jacob et al., 1997; Stevenson et al., 1998; Dentener et al., 1999; Rasch et al., 2000; Taguchi et al., 2002; Chevillard et al., 2002; Collins et al., 2002). In this context, a uniform $^{222}$Rn source term of $-1$ atom cm$^{-2}$ s$^{-1}$ from all ice-free land surfaces is generally assumed. This value is between the global mean estimates of 0.72 atom cm$^{-2}$ s$^{-1}$ (Lambert et al., 1982) and 1.2 atom cm$^{-2}$ s$^{-1}$ (Turekian et al., 1977), and is thought to be accurate to within 25% globally and a factor of 2 regionally (Jacob et al., 1997, and references therein). In an attempt improve model predictions of atmospheric $^{222}$Rn concentrations, some workers have modified this uniform $^{222}$Rn flux distribution so as to take into account some of the variability in $^{222}$Rn emissions. For example, Lee and Feichter (1995) assumed a reduced source strength of 0.005 atom cm$^{-2}$ s$^{-1}$ between 60 and 70°N, to account for apparent snow cover and soil freezing effects, and found that this improved model predictions of $^{210}$Pb deposition rates. This source distribution was also used in the 1993 World Climate Research Program (WCRP) sponsored intercomparison of global atmospheric transport models (Jacob et al., 1997), and a similar modification (0.5 atom cm$^{-2}$ s$^{-1}$ between 60 and 70°N) was made in the 1995 WCRP workshop (Rasch et al., 2000). Other modifications of the $^{222}$Rn source term which have been used include: accounting for a small oceanic flux (Heimann et al., 1990; Taguchi et al., 2002); taking into account variations in emissions due to soil texture (Dentener et al., 1999; Chevillard et al., 2002) and snow cover (Dentener et al.,
Some have also tried to improve $^{222}$Rn predictions by taking into account temporal changes in $^{222}$Rn flux (Jacob and Prather, 1990; Lin et al., 1996; Genthon and Armengaud, 1995). However, where any effects of these spatial and temporal modifications on predicted concentrations has been found, they have generally not been quantified.

Recently, a more far-reaching modification in the global $^{222}$Rn flux term has been proposed by Conen and Robertson (2002). It is based on an empirical relationship between $^{222}$Rn emissions and latitude which has been derived from published indirect $^{222}$Rn flux measurements and estimates calculated from $^{210}$Pb fluxes. With this emissions distribution, the $^{222}$Rn flux is 1 atom cm$^{-2}$ s$^{-1}$ between 60°S to 30°N, and from there on decreases linearly to 0.2 atom cm$^{-2}$ s$^{-1}$ at 70°N. $^{222}$Rn emissions are expected to decrease with increasing latitude in the Northern Hemisphere as a result of the increasing proportion of wetlands and organic soils (Stillwell-Soller et al., 1995; Conen and Robertson, 2002). Only $^{222}$Rn produced in aerated surface layers of the soil is likely to escape to the atmosphere before its decay. Regional gradients in soil $^{226}$Ra content caused by geochemical weathering patterns may also contribute to this trend, as appears to be the case in China, where concentrations of $^{222}$Rn precursors decrease from south to north (Xu et al., 1993; Sun et al., 2004). South of 60°S and north of 70°N, $^{222}$Rn emissions are assumed to be zero. However, small fluxes (0.077 atom cm$^{-2}$ s$^{-1}$) have been reported at 62°S during the brief Antarctic summer (Evangelista and Pereira, 2002).

In this paper, we present the results of a study to find if this new source term improves predictions of $^{222}$Rn compared to using the uniform $^{222}$Rn source term of 1 atom cm$^{-2}$ s$^{-1}$ between 60°S and 70°N. The observational data used were long-term average $^{222}$Rn concentrations for 23 ground-based stations and two averaged vertical profiles. The model used was STOCHEM-Ed (Stevenson et al., 2003), a new version of the UK Met Office global chemistry-transport-model (CTM), first described in Collins et al. (1997).
7.3 Observations, model and simulations

7.3.1 Surface observations
The data used for surface comparisons were published monthly mean $^{222}$Rn concentrations available for 22 sites located at different latitudes, and data for the Cape Grim Baseline Air Pollution Station (W. Zahorowski, personal communication). The locations of these stations are shown in Figure 7.1, and details of each site are summarised in Table 7.1. Station locations range in latitude from 68°N (Pallas, Finland) to the South Pole, with 13 stations north of 30°N and 10 stations south of 30°N. Long-term means of surface $^{222}$Rn concentrations were calculated from reported monthly means, except for Mauna Loa and Bermuda, where published values were monthly medians. For Pallas and New York City, where $^{222}$Rn concentrations have been published for more than one height, we choose the greatest available height as the most representative of the concentrations in the lowest layer in our model. For Pallas this was Sammaltunturi station, which is on a hill side 565 m above sea level and around 200 m

![Figure 7.1](image.png)
Table 7.1. Location of stations where measurements of atmospheric $^{222}\text{Rn}$ concentrations have been performed for durations of more than 2 months.

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>Station</th>
<th>Type</th>
<th>Period of observation</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.0° N</td>
<td>24.1° E</td>
<td>Pallas, Finland</td>
<td>polar</td>
<td>7 years</td>
<td>Hatakka et al. (2003)</td>
</tr>
<tr>
<td>65.6° N</td>
<td>168.0° W</td>
<td>Wales, Alaska</td>
<td>coastal</td>
<td>7 years</td>
<td>Lockhart (1962)</td>
</tr>
<tr>
<td>57.8° N</td>
<td>152.5° W</td>
<td>Kodiak, Alaska</td>
<td>marine</td>
<td>11 years</td>
<td>Lockhart (1962)</td>
</tr>
<tr>
<td>56.5° N</td>
<td>32.9° E</td>
<td>Fyodorowskoye, Russia</td>
<td>continental</td>
<td>Mar + Jul + Oct, 1 year</td>
<td>Chevillard et al. (2002)</td>
</tr>
<tr>
<td>54.4° N</td>
<td>12.7° E</td>
<td>Zingst, Germany</td>
<td>coastal</td>
<td>Mar + Jul + Oct, 1 year</td>
<td>Chevillard et al. (2002)</td>
</tr>
<tr>
<td>53.3° N</td>
<td>9.9° W</td>
<td>Mace Head, Ireland</td>
<td>coastal</td>
<td>Jun-Aug, 2 years</td>
<td>Braud et al. (2002)</td>
</tr>
<tr>
<td>49.4° N</td>
<td>8.9° E</td>
<td>Heidelberg, Germany</td>
<td>continental</td>
<td>Mar + Jul + Oct, 1 year</td>
<td>Chevillard et al. (2002)</td>
</tr>
<tr>
<td>47.9° N</td>
<td>7.9° E</td>
<td>Schauinsland, Germany</td>
<td>continental</td>
<td>4.5 years</td>
<td>Schmidt et al. (1996)</td>
</tr>
<tr>
<td>46.6° N</td>
<td>8.0° E</td>
<td>Jungfrau, Switzerland</td>
<td>continental</td>
<td>1 year</td>
<td>Gächter et al. (1995)</td>
</tr>
<tr>
<td>40.7° N</td>
<td>73.9° W</td>
<td>New York City</td>
<td>coastal</td>
<td>2 years</td>
<td>Fisenne and Keller (1996)</td>
</tr>
<tr>
<td>40.0° N</td>
<td>84.0° W</td>
<td>Cincinnati, Ohio</td>
<td>continental</td>
<td>4 years</td>
<td>Gold et al. (1964)</td>
</tr>
<tr>
<td>35.3° N</td>
<td>139.7° E</td>
<td>Yokosuka, Japan</td>
<td>coastal</td>
<td>4.5 years</td>
<td>Lockhart (1959)</td>
</tr>
<tr>
<td>32.3° N</td>
<td>64.9° W</td>
<td>Tudor Hill, Bermuda</td>
<td>marine</td>
<td>4 years</td>
<td>EML (2003)</td>
</tr>
<tr>
<td>19.5° N</td>
<td>155.6° W</td>
<td>Mauna Loa, Hawaii</td>
<td>marine</td>
<td>3 years</td>
<td>Hutter et al. (1995)</td>
</tr>
<tr>
<td>12.0° S</td>
<td>77.0° W</td>
<td>Lima, Peru</td>
<td>coastal</td>
<td>1 year</td>
<td>Lockhart (1960)</td>
</tr>
<tr>
<td>15.7° S</td>
<td>67.6° W</td>
<td>Chacaltaya, Bolivia</td>
<td>continental</td>
<td>1.5 years</td>
<td>Lockhart (1960)</td>
</tr>
<tr>
<td>23.0° S</td>
<td>43.2° W</td>
<td>Rio de Janeiro, Brazil</td>
<td>coastal</td>
<td>2 years</td>
<td>Lockhart (1960)</td>
</tr>
<tr>
<td>40.4° S</td>
<td>144.4° E</td>
<td>Cape Grim, Tasmania</td>
<td>coastal</td>
<td>15 years</td>
<td>W. Zahorowski (pers. com.)</td>
</tr>
<tr>
<td>46.0° S</td>
<td>51.0° E</td>
<td>Crozet Island</td>
<td>marine</td>
<td>27 years</td>
<td>Lambert et al. (1995)</td>
</tr>
<tr>
<td>54.5° S</td>
<td>159.0° E</td>
<td>Macquarie Island</td>
<td>marine</td>
<td>Apr + Nov, 2 years</td>
<td>Whittlestone and Zahorowski (1998)</td>
</tr>
<tr>
<td>70.6° S</td>
<td>8.4° W</td>
<td>Georg v. Neumayer station, Antarctica</td>
<td>polar</td>
<td>6 years</td>
<td>Wyputta (1997)</td>
</tr>
<tr>
<td>78.2° S</td>
<td>162.2° W</td>
<td>Little America V, Antarctica</td>
<td>polar</td>
<td>2.5 years</td>
<td>Lockhart (1960)</td>
</tr>
<tr>
<td>90.0° S</td>
<td></td>
<td>South pole</td>
<td>polar</td>
<td>1 year</td>
<td>Lockhart (1960)</td>
</tr>
</tbody>
</table>

*In Jacob et al. (1997)
above the surrounding area, and for New York City this was 260 m above street level. By averaging over the longest time-scale available, much of the temporal variation in \(^{222}\text{Rn}\) concentrations is eliminated (Robé et al., 1992). Thus, comparisons with predictions become less subject to the ability of the model to faithfully reproduce temporal variations in \(^{222}\text{Rn}\) concentrations, and a larger proportion of any discrepancy between prediction and observations becomes attributable to the differences between the actual and assumed \(^{222}\text{Rn}\) source terms or systematic deficiencies in the model. One measure of the discrepancy between prediction and observation we have used is the average of prediction/observation ratios; the other is the root-mean-square error of prediction relative to observation.

### 7.3.2 Vertical profile observations

The vertical profile data used were those published in Kritz et al. (1998) and Zaucker et al. (1996). These data are the most recent, reliable and detailed \(^{222}\text{Rn}\) profile data available. The data in Kritz et al. (1998) were collected in the vicinity of Moffet Field, California, USA (~38°N, 122°W). Measurements were made during the period from June 3rd to August 16th 1994 and consisted of 11 flights up to 11.5 km altitude. The data in Zaucker et al. (1996) were collected over Nova Scotia, New Brunswick, and the western North Atlantic Ocean (~44°N, 64°W), with flights originating from Halifax. These measurements were made between the 16th and 31st August 1993 as part of the North Atlantic Regional Experiment (NARE) campaign, and consisted of 9 flights up to 5500 m. For each data set, an average \(^{222}\text{Rn}\) profile was compiled from the separate flights by averaging measured values over 1000 m intervals, and 2000 m intervals for greater altitudes. No interpolation was made. The measurements were compared to the model layers corresponding to the same height intervals.
7.3.3 Model

STOCHEM-Ed is a new version of the UK Met Office three-dimensional Lagrangian CTM STOCHEM (e.g. Collins et al., 1997, 2000, 2002), developed at the University of Edinburgh. STOCHEM-Ed is closely coupled to the Unified Model (UM) general circulation model (GCM) (Johns et al., 1997), from which it is receiving meteorological fields every 3 hours. Earlier versions of STOCHEM have taken part in a number of inter-comparisons regarding transport and chemistry, including the 1995 WRCP workshop (Rasch et al., 2000). In all of these studies the model was typically found to perform well within the range of other current models. Thus, we would expect the results of this study to also be valid for other global atmospheric models, although this should be tested.

STOCHEM-Ed uses a Lagrangian transport scheme, dividing the atmosphere into 50000 equal mass air parcels. These parcels are advected by winds from the GCM with a 4th order Runge-Kutta algorithm, using linear horizontal interpolation and cubic vertical interpolation, and adding a small random walk component to simulate turbulent diffusive mixing. The parcels maintain an approximately even global distribution with time. Convective mixing is implemented by fully mixing a fraction of the parcels beneath a convective cloud top. The precipitation rate and fractional cloud cover determine the amount mixed (Stevenson et al., 1998). Inter-parcel mixing occurs between parcels occupying the same grid-box after each 1-h advection step. Turbulent mixing in the boundary layer is achieved by randomly re-assigning the vertical co-ordinates of air parcels over the depth of the layer. The grid used for mixing is 5° by 5°, with 22 vertical hybrid (\( \eta \)) levels (6 levels with \( \Delta \eta=0.1 \) between \( \eta=1.0 \) and \( \eta=0.4 \), 15 levels with \( \Delta \eta=0.025 \) between \( \eta=0.4 \) and \( \eta=0.025 \), and a top level between \( \eta=0.025 \) and \( \eta=0.0003 \)). Hybrid co-ordinates are explained further in Collins et al. (1997), but can be considered as approximately equal to pressure divided by surface pressure. The surface boundary layer vertical resolution in STOCHEM-Ed is quite
coarse, with the lowest six levels being approximately 100 hPa thick (~1 km). The boundary layer is therefore typically represented by only one or two levels. The top level is in the stratosphere, well above the highest level of interest for $^{222}$Rn (approximately tropopause levels). The driving GCM has a more highly resolved boundary layer, which is represented by 6 different levels. Surface trace gas emissions are added to air parcels within the boundary layer above their sources. Gridded emission distributions with a horizontal resolution of $5^\circ \times 5^\circ$ are used. When several air parcels occupy the boundary layer for the grid square, emissions are divided equally between them. If no air parcels are present, for example when the boundary layer is very shallow, emissions are stored until the next time-step, ensuring mass conservation. A more detailed description of STOCHEM-Ed can be found in Stevenson et al. (2003).

7.3.3 Simulations

For each $^{222}$Rn source term one 15-month simulation was carried out, the first three months of which were discarded as spin-up time. The meteorological driver (UM) was configured as an atmosphere-only GCM, with a resolution of 3.75° longitude by 2.5° latitude and with 58 vertical levels between the surface and 0.1 hPa. Recent climatologies of sea-surface temperatures and stratospheric ozone were used to drive the GCM. The modelled values of $^{222}$Rn for each station are linearly interpolated from the four surrounding grid-boxes, where the values for a grid box are taken to be representative of its central latitude and longitude. These grid boxes are illustrated in Figure 1a. For all stations except Mauna Loa (3400 m asl) and Jungfraujoch (3580 m asl) the $^{222}$Rn concentrations used in the comparison were for the lowest model layer. For Mauna Loa this was the second layer. At Jungfraujoch, strong diurnal variations in $^{222}$Rn with maxima during late afternoon in summer, and the absence of variations in winter, indicate the influence of the convective boundary layer in summer and exposure to the free troposphere in winter (Gäggeler et al., 1995). Thus, for Jungfraujoch we used model layer 2 (centered 1200 m above local ground surface) for
June to September, and model layer 3 (centered 2000 m above local ground surface) the rest of the year.

7.4 Results and discussion
The assumption of a decreasing $^{222}$Rn source strength north of 30°N only notably affected predicted $^{222}$Rn concentrations in the Northern Hemisphere (Table 7.2), as we would expect given the mean atmospheric (or e-folding) life-time of $^{222}$Rn of 5.5 days. Differences in atmospheric $^{222}$Rn concentrations between the two simulations were

Table 7.2. Observed and predicted long-term $^{222}$Rn concentrations (Bq m$^{-3}$) for two different $^{222}$Rn source term assumptions.

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Station</th>
<th>Observation</th>
<th>Prediction</th>
<th>Prediction/observation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Uniform</td>
<td>Northwards-decreasing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Uniform</td>
<td>Northwards-decreasing</td>
</tr>
<tr>
<td>68.0°N</td>
<td>Pallas</td>
<td>1.22</td>
<td>1.54</td>
<td>0.43</td>
</tr>
<tr>
<td>65.6°N</td>
<td>Wales</td>
<td>0.74</td>
<td>0.98</td>
<td>0.25</td>
</tr>
<tr>
<td>57.8°N</td>
<td>Kodiak</td>
<td>0.36</td>
<td>1.94</td>
<td>0.51</td>
</tr>
<tr>
<td>56.5°N</td>
<td>Fyodorowskoye</td>
<td>1.45</td>
<td>4.62</td>
<td>1.44</td>
</tr>
<tr>
<td>54.4°N</td>
<td>Zingst</td>
<td>1.33</td>
<td>3.27</td>
<td>1.24</td>
</tr>
<tr>
<td>53.3°N</td>
<td>Mace Head</td>
<td>0.44</td>
<td>1.44</td>
<td>0.53</td>
</tr>
<tr>
<td>49.4°N</td>
<td>Heidelberg</td>
<td>4.13</td>
<td>3.31</td>
<td>1.45</td>
</tr>
<tr>
<td>47.9°N</td>
<td>Schauinsland</td>
<td>2.02</td>
<td>3.17</td>
<td>1.48</td>
</tr>
<tr>
<td>46.6°N</td>
<td>Jungfraujoch</td>
<td>0.58</td>
<td>0.81</td>
<td>0.42</td>
</tr>
<tr>
<td>40.7°N</td>
<td>New York City</td>
<td>3.40</td>
<td>3.25</td>
<td>1.78</td>
</tr>
<tr>
<td>40.0°N</td>
<td>Cincinnati</td>
<td>5.04</td>
<td>3.71</td>
<td>2.23</td>
</tr>
<tr>
<td>35.3°N</td>
<td>Yokusuka</td>
<td>2.06</td>
<td>2.12</td>
<td>0.97</td>
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<tr>
<td>32.3°N</td>
<td>Tudor Hill</td>
<td>0.46</td>
<td>0.59</td>
<td>0.36</td>
</tr>
<tr>
<td>19.5°N</td>
<td>Mauna Loa</td>
<td>0.18</td>
<td>0.11</td>
<td>0.07</td>
</tr>
<tr>
<td>12.0°S</td>
<td>Lima</td>
<td>1.15</td>
<td>1.94</td>
<td>1.94</td>
</tr>
<tr>
<td>15.7°S</td>
<td>Chacaltaya</td>
<td>1.44</td>
<td>2.64</td>
<td>2.64</td>
</tr>
<tr>
<td>23.0°S</td>
<td>Rio de Janeiro</td>
<td>1.52</td>
<td>1.28</td>
<td>1.28</td>
</tr>
<tr>
<td>40.4°S</td>
<td>Cape Grim</td>
<td>0.68</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>46.0°S</td>
<td>Crozet Island</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>54.5°S</td>
<td>Macquarie Island</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>70.6°S</td>
<td>Georg v. Neumayer</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>78.2°S</td>
<td>Little America V</td>
<td>0.10</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>90.0°S</td>
<td>South pole</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
largest in the surface layer polewards of 40°N, with peak differences towards the centre of large land masses (Canada and Siberia). In relative terms, the northwards-decreasing source term resulted in a reduction of more than 70% in surface layer concentrations northwards of 60°N (Figure 7.2). This difference between the two simulations decreased steadily with decreasing latitude, and at 30°N was less than 10% over the continents and less than 30% over the centre of the oceans.

Figure 7.2. The relative change (%) in $^{222}$Rn concentrations when changing to the northwards-decreasing emissions distribution.

In this study, the approach taken to comparing predictions to observations is somewhat different from that of previous studies. For each site, predictions and observations have been averaged over the longest time-scale available, without taking into account variations over shorter time scales (e.g.: Dentener et al., 1999; Taguchi et al., 2002). This way, the influence of random errors in the comparison, for both observations and predictions, has been reduced. We did not attempt to judge the quality of the measurements reported, assuming instrumental bias is distributed randomly among the
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23 stations and averages zero. Using the largest number of stations possible should then result in the smallest bias in the overall judgment. If the model is a perfect representation of reality and bias among the stations is distributed as assumed, we would expect prediction and observation to converge towards the same value with increasing averaging time and increasing number of stations included in the comparison. If this is not the case, systematic deficiencies of the model, the observations, or both, could be responsible. However, currently, the most important systematic uncertainty in matching predictions with observations seems to be uncertainties in $^{222}\text{Rn}$ emissions (Schery and Wasiolek, 1998; Chevillard et al., 2002); thus, the similarity of predicted and observed long-term averages at a large number of stations should be an indication of the accuracy of the $^{222}\text{Rn}$ source term employed.

Globally, the northwards-decreasing $^{222}\text{Rn}$ source term resulted in a mean prediction/observation ratio (0.82) closer to unity than the uniform source term assumption (1.49) (Table 7.3). Also, the root-mean-square error was smaller: 0.49 for the northwards-decreasing source term compared to 1.22 for the uniform source term assumption. However, when we take a more differentiated look we find that this improvement was mainly due to an improvement in prediction at stations north of 50°N, where predictions were improved at four out of six stations. For stations north of 50°N the uniform source term resulted in an almost three-fold (2.80) over-estimation, whereas

<table>
<thead>
<tr>
<th>Geographic coverage</th>
<th>No. of stations</th>
<th>Mean prediction/observation ratio</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uniform</td>
<td>Northwards-decreasing</td>
</tr>
</tbody>
</table>
| North of 50°N       | 6              | 2.80    | 0.87                | 2.27    | 0.42                  
| 30°N-50°N           | 7              | 1.11    | 0.58                | 0.31    | 0.45                  
| South of 30°N       | 10             | 0.97    | 0.96                | 0.53    | 0.55                  
| Global              | 23             | 1.49    | 0.82                | 1.22    | 0.49                  

Table 7.3. Surface data mean prediction/observation ratios and root-mean-square-error of prediction relative to observation (RMSE) for three areas of geographic coverage.
predictions based on the northwards decreasing source term were relatively close to unity (0.87). Yet, in the latitudinal band between 30°N to 50°N, predictions based on the uniform source term were closer to observations at four out of seven stations and mean prediction/observation ratios were much closer to unity (1.11) than for predictions based on the northwards decreasing source term (0.58). South of 30°N, little difference was found between the two sets of predictions. In both cases, mean prediction/observation ratios were close to unity (0.97; 0.96) and the root-mean-square error was slightly over 0.5. This last result gives some confidence in the model not being particularly biased towards under- or over-estimation. Thus, for our comparison of different 222Rn source terms we can suppose that both the better results north of 50°N as well as the under-estimate between 30°N and 50°N for the northwards decreasing source term assumption are likely to be genuine.

Predicted and observed 222Rn concentrations for the two vertical profiles are shown in Figure 7.3. Mean 222Rn concentrations were greater for the Nova Scotia/North Atlantic Ocean profile (Zaucker et al., 1996) than for the Californian profile (Kritz et al., 1998), despite the fact that air samples for the first profile were largely collected over the ocean. However, given the predominantly westerly winds at these latitudes, west coast locations are likely to be more strongly influenced by 222Rn-poor maritime air, and east coast locations more strongly influenced by 222Rn-rich continental air, and thus 222Rn concentrations will tend to be greater on the east coast of the continent. The largest differences in absolute terms between the two sets of predicted concentrations occur in the surface layer, as we would expect. In relative terms, however, the decrease was as large or larger at higher levels. The differences are greater for the Nova Scotia profile than for the California profile because of the higher latitude of this region (Figure 7.3). At 44°N (the latitude of the Nova Scotia profile) the northwards-decreasing source term assumes 28% less emissions, but only 16% less at 38°N (the latitude of the Californian profile).
Figure 7.3. Observed and predicted $^{222}\text{Rn}$ concentrations for: (a) the California region, and (b) the Nova Scotia and North Atlantic Ocean region. Observed concentrations are the average from all flights made during the measurement campaign.

Mean prediction/observation ratios and the root-mean-square error of prediction relative to observation for each profile are given in Table 7.4. For the Nova Scotia data there was substantial improvement in model predictions when changing to the northwards-decreasing $^{222}\text{Rn}$ source term, especially at heights above 2000 m. The mean prediction/observation ratio for all height intervals altered from 1.40 to 0.72, and the

Table 7.4. Vertical profile mean prediction/observation ratios and root-mean-square-errors of prediction relative to observation (RMSE).

<table>
<thead>
<tr>
<th>Region</th>
<th>No. of height intervals</th>
<th>Mean prediction/observation ratio</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uniform</td>
<td>Northwards-decreasing</td>
</tr>
<tr>
<td>Nova Scotia</td>
<td>6</td>
<td>1.40</td>
<td>0.72</td>
</tr>
<tr>
<td>California</td>
<td>16</td>
<td>1.04</td>
<td>0.69</td>
</tr>
</tbody>
</table>
root-mean-square error of prediction relative to observation was reduced from 0.52 to 0.33. Changing to the northwards-decreasing $^{222}$Rn source term shifted the mean prediction/observation ratio away from unity for the California profile, but predictions were improved for the lowest two height intervals. Similar results to this (improved prediction for the Nova Scotia profile but no improvement for the California profile) have been found by Gupta et al. (2004), in a study in which they compared the northwards-decreasing source term to the source term used in the 1993 WCRP workshop (Jacob et al., 1997). As for the results for the surface data, this observation suggests that the northwards-decrease in $^{222}$Rn source strength begins somewhat north of 30°N.

7.5 Conclusions

The comparison of observed and predicted $^{222}$Rn concentrations lends, in general, support to the assumption of a decrease in $^{222}$Rn source strength with increasing latitude in the Northern Hemisphere. Empirical evidence based on indirect $^{222}$Rn flux measurements and estimates derived from $^{210}$Pb fluxes suggests that fluxes decrease northwards of 30°N. However, the validation of this suggestion through comparison of predicted and observed atmospheric $^{222}$Rn concentrations yielded mixed results. While the northwards-decreasing source term substantially improved predictions north of 50°N compared to a uniform source term of 1 atom cm$^{-2}$ s$^{-1}$, it also resulted in a systematic under-prediction of $^{222}$Rn concentrations in the latitudinal band between 30°N and 50°N, a region where predictions based on the uniform source term were closer to observations. Although this study does not provide a proof of one particular source term it indicates that the northwards-decreasing source term is a more realistic representation than the generally-used uniform 1 atom cm$^{-2}$ s$^{-1}$ source term. It also suggests that this decrease begins somewhere between 30°N and 50°N, rather than at 30°N as indicated by the available flux measurements. Future investigations into $^{222}$Rn fluxes should therefore concentrate on these latitudes. Whilst this study suggests a geographic region where further refinement might be necessary, appropriate investigation needs to be made by
other means, otherwise the derived source term will not be model-independent and therefore cannot be used in future model validations. Guidance for further improvement of $^{222}\text{Rn}$ parameterisation has recently been worked out in an expert meeting supported by the World Meteorological Organisation / Global Atmosphere Watch (WMO, 2004). This includes, amongst others, the quest for quality controlled measurements of $^{222}\text{Rn}$ emissions along North-South transects in Europe and North America, and improved knowledge of global surface $^{226}\text{Ra}$ concentrations.
8.1 The significance of atmospheric applications of $^{222}\text{Rn}$ and $^{220}\text{Rn}$

$^{222}\text{Rn}$, $^{220}\text{Rn}$ and their decay products – and a number of radionuclides present in the atmosphere, such as cosmogenic $^7\text{Be}$, $^{10}\text{Be}$ and $^{14}\text{C}$ – have been used as atmospheric tracers for many years, but it is only over the last decade or so, with the expansion of global monitoring networks, that the full potential of these isotopes as tools for studying atmospheric processes has been recognized and begun to be exploited more fully. In June 2003, the first international expert meeting on the ‘Sources and Measurements of Natural Radionuclides Applied to Climate and Air Quality Studies’ was held at Gif sur Yvette, France. Two of the main recommendations to come from this meeting were that more systematic surveys of $^{222}\text{Rn}$ flux are needed, and that a more globally-integrated approach to measurements, data quality assurance and archiving should be developed (WMO, 2004).

Currently, the most prominent atmospheric applications of $^{222}\text{Rn}$ are the evaluation of atmospheric transport models and estimation of regional-scale ($10^2$ to $10^5$ km$^2$) fluxes of climatically sensitive gases such as CO$_2$, N$_2$O and CH$_4$. With substantial improvements in model resolutions over the last decade or so, and the expansion of the global network of $^{222}\text{Rn}$ observations, it has become possible to carry out increasingly detailed model evaluation studies, for example, Chevillard et al. (2002) have recently carried out the first validation of a mesoscale model (REMO). The use of spatially undifferentiated
$^{222}\text{Rn}$ source terms and the limited amount of $^{222}\text{Rn}$ profile data are limiting these studies, and thus the accuracy of air quality and climate modelling studies.

$^{222}\text{Rn}$-tracer methods of measuring trace gas fluxes have the potential to substantially improve the long-term monitoring trace gas fluxes on the local and regional scales. Used on the regional scale (integrating over time during a synoptic or nocturnal inversion, e.g. Kuhlmann et al., 1998), the $^{222}\text{Rn}$ tracer method offers a much cheaper alternative to other techniques available for estimating fluxes on this scale. Boundary layer budget methods (e.g. Denmead et al., 1996; Levy et al., 1999) require accurate estimates of the boundary layer height, which are expensive to obtain (e.g. radiosondes, acoustic sounding, profiles of atmospheric constituents measured from aircraft). Eddy covariance measurements made from aircraft (e.g. Gioli et al., 2004) are also expensive. As the $^{222}\text{Rn}$-tracer method does not require the boundary layer height (by scaling the flux of the gas of interest to that of $^{222}\text{Rn}$ the boundary layer height is no longer required – Eq. 2.5), it provides a much cheaper alternative to these other methods. However, as the error in the estimate of the target gas is directly proportional to the error in the $^{222}\text{Rn}$ source term used (Eq. 2.5), the accuracy of $^{222}\text{Rn}$-based flux estimates are directly dependent on the accuracy of the $^{222}\text{Rn}$ source term used.

$^{222}\text{Rn}$ is also increasingly being used to estimate trace gas fluxes on the local scale (0.1 to 10 ha). Used in this way (integrating over height, e.g. Conen et al., 2002), the $^{222}\text{Rn}$ tracer method is particularly useful as it can be used under light wind or stable conditions, when most micrometeorological methods (e.g. aerodynamic methods or the Bowen-ratio method) are not valid, as conventional models of atmospheric dispersion are no longer applicable under these conditions (Butterweck et al., 1994; Mahrt, 1998). This point also applies to the use of $^{220}\text{Rn}$ to calculate the turbulent diffusivity ($K$) of the near-surface boundary layer (e.g. Butterweck et al., 1994). More sophisticated approaches to measuring trace gas fluxes at this scale, such as the eddy covariance
method (e.g. Moncrieff et al., 1997; Soegaard et al., 2003) involve large experimental
effort, and have large analysis requirements. The radon tracer method is also attractive
in that it can easily be automated, and it permits the calculation of smaller fluxes on the
field scale; these fluxes (e.g. N₂O and CH₄) cannot be readily detected using
micrometeorological methods, except for when complex tunable diode laser systems are
used. Also, there are particular environments in which the ²²²Rn-tracer method could be
exploited to provide a much better understanding of trace gas budgets for that
ecosystem. One example is the under-canopy of forests (e.g. Martens et al., 2004),
where conventional models of atmospheric dispersion, and thus micrometeorological
methods, are generally not applicable. Another is in regions where termites produce
large and very localised emissions of CH₄ in an area which is otherwise a CH₄ sink (e.g.
MacDonald et al., 1998). As it is difficult to measure CH₄ emissions by chambers in this
situation, the ²²²Rn tracer method could prove to be extremely useful (but this does not
appear to have been attempted).

As the foregoing discussion indicates, atmospheric applications of ²²²Rn and ²²⁰Rn can
contribute significantly to atmospheric science. Accurate estimates of the magnitude of
trace gas fluxes are needed for national emissions inventories (which are now legally
required in countries which have signed the Kyoto Treaty), and in climate and air quality
studies, which are carried out using atmospheric transport models which have often been
validated and parameterised using ²²²Rn. For example, regional-scale trace gas fluxes
are increasingly being derived by inverse modelling (e.g. Gurney et al., 2002; Gimson
and Uliaasz, 2003). However, in order to exploit the full potential of ²²²Rn and ²²⁰Rn as
atmospheric tracers, improved information on the spatial and temporal distribution in
their emissions is essential. The overall aim of this research was to improve on the
current state of knowledge on the temporal and spatial distribution of ²²²Rn and ²²⁰Rn
emissions, so that these isotopes and their decay products can be used more effectively
in atmospheric applications. The main contributions of this thesis are summarised below.

### 8.2 Contributions of this thesis

The overall aim of this research was to improve on the current state of knowledge on the temporal and spatial distribution of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ emissions, so that these isotopes and their decay products can be used more effectively in atmospheric applications. In particular, this research has focused on the measurement of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ emissions from soils, and investigations of the temporal and spatial variability in these emissions on various scales, and the factors which control this variability. These studies have contributed to the limited number studies of $^{222}\text{Rn}$, and especially, $^{220}\text{Rn}$ emissions, and have shed new light on some of the factors which control their emission rate from soils for which there is little information available, such as water table depth, freezing of the soil, and snow cover. Understanding the factors which control the temporal and spatial variability in radon emissions is important for modelling emissions, but it also important from a sampling perspective i.e. so sampling can be optimised to provide accurate source terms. The findings of these studies and their implications for atmospheric tracer studies are discussed in more detail below in §8.3.

Throughout this work, $^{222}\text{Rn}$ and $^{220}\text{Rn}$ fluxes have been measured by the closed (or static) chamber method, using a commercially available radon monitor (Genitron Instrument’s AlphaGUARD) for radon detection. This approach is novel in that a single AlphaGUARD instrument has been used to measure both the $^{222}\text{Rn}$ and $^{220}\text{Rn}$ flux simultaneously, and thus provides a more economical alternative to the method of Lehmann et al. (2004), which uses two instruments. An automated system for the analysis of $^{222}\text{Rn}$ in air samples has also developed. This has enabled studies of the spatial variation in $^{222}\text{Rn}$ emissions in which measurements were independent of time for, as far as is known, the first time.
Methods of predicting the spatial distribution of $^{222}$Rn emissions and improving on current $^{222}$Rn source terms used in models have been explored as part of this research—namely, the use of gamma dose rate as a proxy; modelling emissions using digital soils and geology data; and modifying the uniform 1 atom cm$^{-2}$ s$^{-1}$ $^{222}$Rn source term generally assumed in modelling studies to account for a trend of decreasing $^{222}$Rn emissions with increasing latitude in the Northern Hemisphere. These methods and some other approaches of providing spatially and temporally resolved descriptions of $^{222}$Rn emissions are discussed in more detail below in §8.4.

This research also has value in the fields of radon risk mapping, and epidemiological studies of the occurrence of lung cancer and other illnesses which have been connected to high exposures to radon. Currently, identifying regions at risk of high radon concentrations occurring indoors is carried out using a combination of indoor $^{222}$Rn concentrations, geology maps, gamma surveys, and soil gas concentrations and soil permeability measurements. Maps of $^{222}$Rn emissions would clearly be useful in this context, and would be welcomed by epidemiologists, as these investigations are generally limited by the lack of data on the spatial distribution of radon emissions (Badr, 1993). Also, given the large horizontal, vertical, and temporal variability in soil gas concentrations, it is possible that radon fluxes could be better predictors of high concentrations indoors. Neznel and Neznel (2002b) have investigated this in the Czech Republic, and found that $^{222}$Rn flux was not a better predictor than soil gas concentrations; however, this is only one study.

8.3 Temporal and spatial variability of radon emissions

Studies of the temporal variation in radon emissions undertaken in this project have confirmed that soil moisture is the most important factor affecting radon emissions, and that heavy rainfall may temporarily completely interrupt radon emissions if the soil surface becomes completely saturated (§4.4.1). Water table depth ($z''$), a factor which
does not appear to have been included in investigations of radon emissions previously, was also found to be an important factor controlling $^{222}\text{Rn}$ emissions when $z^w$ is greater than $z^d$, the relaxation depth of radon in the soil (§2.2.2). $z^w$ is not an important for $^{220}\text{Rn}$ emissions, however, because of the much shorter diffusion length, and thus $z^d$ for this nuclide.

Atmospheric pressure, which has previously been found to be an important factor affecting radon emissions at sites with porous and fractured soils (Schery et al., 1982, 1984), or during times when there was no rainfall (Koarashi et al., 2000), was not found to be an important factor in this research. This was not unexpected, however, given the generally high moisture content of the soil and water table depths of the study area. Kojima (1998) demonstrated that variations in the pressure difference between the soil surface and at depth were correlated with a diurnal pattern in $^{222}\text{Rn}$ emissions of peak emissions in the afternoon and a minimum in the early morning, and attributed this to the diurnal pattern in atmospheric turbulence. $^{222}\text{Rn}$ emissions were found to follow a similar pattern to this on a small number of rainfall-free days (n=4) during the summer short-term study (§4.3.1). It is possible that this trend could also have been caused by the diurnal pattern in atmospheric turbulence; however, given the relatively high soil moisture content and water table depth at this site (the mean soil moisture content during this study was 0.34 m$^3$ m$^{-3}$, and the mean water table depth was 0.57 m – Table 4.1), the diurnal cycle in evapotranspiration is more likely to be the cause. The diurnal variation of radon emissions is clearly a topic which needs to be investigated in more detail, as it is generally assumed (presumably on the basis that radon is produced by a purely physical process) that radon emissions do not have a diurnal cycle (and thus the time of day that radon flux measurements are made is generally not considered to be a sampling issue).
Soil temperature was not found to be a significant factor affecting radon emissions in this research. Although many studies have reported a significant correlation between radon flux and soil temperature (e.g. Schery et al., 1989; Dueñas et al., 1997; Koarashi et al., 2000), and higher temperatures will cause an increase in radon emissions because of enhanced diffusion and thermal expansion of soil air, these effects are generally of minor importance over the range of temperatures found in the environment (Schery et al., 1989). Changes in the solubility of radon in soil water will also be affected by temperature; however, even over the lower temperature range, where the relative change in solubility is greater, this will not be large enough to have a substantial effect on the radon flux (§4.4.1).

Measurements made when the top 5-6 cm of the soil was frozen have demonstrated that freezing of a surface layer does not cause a significant reduction in emissions. As the reduction in the diffusion coefficient in soil caused by expansion of the soil water on freezing will have only a very small effect on the flux, freezing of the soil should only result in a notable reduction in radon emissions if a significant barrier to diffusion forms, for example, if a closed ice layer develops on the soil surface, or lenses form within the soil (§4.4.1). More measurements are needed to confirm these findings. The effects of snow cover on radon emissions also need to be investigated in more detail. The impact of snow cover will depend on the particular physical characteristics of the snow cover (porosity, tortuosity), and the degree of waterlogging of the soil caused by snow melt. The depth of the snow cover will also be important for $^{220}$Rn emissions. However, it seems likely that because of its relatively large porosity, a fresh and dry snow cover will have minimal impact on the $^{222}$Rn flux (Moriiizumi et al., 2004; Chapter 4), but, depending on its depth, it may cause a substantial reduction the $^{220}$Rn flux (Kataoka et al., 2003). These findings suggest that generalised assumptions of very low or zero emissions from frozen and snow-covered soils need to be re-assessed.
Chapter 8: Discussion and Conclusions

The level of variability in $^{222}$Rn and $^{220}$Rn emissions observed on the day-to-day and seasonal time scales in this research was similar to that reported in other studies (§4.4.2). $^{222}$Rn emissions were normally distributed and coefficients of variation ranged from 24-39%. $^{220}$Rn emissions were approximately log-normally distributed, and the coefficient of variation was 89%. On the seasonal time scale, $^{222}$Rn emissions varied by one third between lowest and highest values. This level of variability is much less than that generally observed for some other surface-emitted gases such as biogenically-produced $N_2O$, $CO_2$ and $CH_4$ (§4.4.2). Thus, despite the variability in emissions, $^{222}$Rn has value as a tracer for these gases.

Investigations of the spatial variability in $^{222}$Rn emissions on the local-scale on one soil type found that emissions were normally distributed, and the level of variability was much less than that of biogenically-produced $N_2O$ (§5.2.1). Again, this comparison illustrates the value of using the $^{222}$Rn-tracer method to estimate field-scale fluxes of $N_2O$ (Conen et al., 2002), as well as other gases which exhibit a large degree of spatial variability such as $CH_4$ (Verchot et al., 1999; MacDonald et al., 1998); given the observed variability, many more flux measurements are required to achieve a specified standard error for $N_2O$ than for $^{222}$Rn (§5.4.1). $^{222}$Rn flux measurements made at 15 sites of different soil type and geology across North Britain showed $^{222}$Rn emissions to be approximately log-normally distributed on the regional-scale, as found in previous investigations (Schery et al., 1989; Nielson et al., 1996). The median $^{222}$Rn flux of 9.7 Bq m$^{-2}$ h$^{-1}$ was considerably lower than estimates of the global mean $^{222}$Rn flux (50-100 Bq m$^{-2}$ h$^{-1}$); however, given the large proportion of peat soils and generally high soil water content and shallow water tables in this region, this is what would be expected (§5.4.1). On the other hand, it is also possible that this value could underestimate the real flux because of a bias towards shallow and peaty soils in this study. The $^{226}$Ra content of the soil was found to be strongly correlated with $^{222}$Rn flux, and to account for most of the variability (~ 80%); however, as measurements were made on medium to
coarse textured soils only, and over a fairly narrow range of soil depths, some of the variability in emissions which would occur due to these factors will have been masked.

8.4 Improving radon source terms

Given the large spatial variability in $^{222}$Rn emissions on the regional-scale (e.g. Schery et al., 1989; Nielson et al., 1996; Chapter 5), mapping radon emissions on the basis of direct measurements is clearly a large (and costly) task, especially as it is also desirable that the seasonal variability in emissions is also taken into account. Hence, a cheaper and more practical solution must be sought. As data on the relevant soil parameters required for adequately modelling emissions (e.g. $^{226}$Ra content, soil moisture content, soil depth, water table depth, particle size distribution, porosity) are currently not adequate for this purpose, the most realistic approach to producing a spatial and temporal description of radon emissions is to combine the two approaches, and to make use of information about the distribution of indirect variables (e.g. soil wetness class, bedrock geochemistry) and variables that could be used as proxies (e.g. $^{226}$Ra content of the soil, gamma dose rate) for which more information is available. Whilst some researchers have combined this approach with porous media transport models (Schery and Wasiolek, 1998; Neilson et al., 1995; Ielsch et al., 2002), the map produced in this research (Chapter 5), and that of Europe by Eckhardt (1990) are purely empirical in nature. Independent $^{222}$Rn flux data are needed to verify these maps, but, given the fairly crude data used as input in these models, it is quite possible that empirical models will perform just as well as those based on a more fundamental mathematical approach. Either way, efforts to improve on or provide an reasonably accurate spatial description of radon emissions on the global and regional scales are currently hampered by the lack of data on the relevant soil parameters – $^{226}$Ra content in particular – and a calibrated set of $^{222}$Rn flux measurements.
Although the $^{226}$Ra content of the soil has been mapped for large areas of the world, either by aerial gamma radiation surveys or soil surveys (e.g. USA, China), there are still large parts of the world where there is no data, including the UK (there is, however, information on the $^{238}$U content of stream sediments for the UK). Aerial gamma spectrometry surveys are an attractive method for obtaining information on the $^{226}$Ra content of the soil as they enable large areas to be covered and produce data much faster than soil sampling. Recent developments such as improved aircraft instrumentation and differential global-positioning systems, and developments in noise-reduction methods have led to a significant improvement in the quality of data now being obtained by aerial gamma radiation surveys (Dickson, 2004); however, they are remain expensive. Thus, for modelling purposes, it is likely that geology maps and information on the concentrations of $^{226}$Ra or $^{238}$U in rocks will have to be relied on for large parts of the world for some time.

Schery (2004) has suggested that north-south $^{222}$Rn flux transects be carried out in Europe and North America, and surveys in other areas where there is already detailed information on the $^{226}$Ra content of the soil. $^{222}$Rn flux measurements should also be concentrated on parts of the world for which there is currently very little data (e.g. Africa, South America), and at higher latitudes in the Northern Hemisphere, in order to verify the trend of decreasing emissions with increasing latitude indicated by indirect flux measurements (Conen and Robertson, 2002/Appendix A/Chapter 5; Robertson et al., 2005/Appendix B/Chapter 7). Given the level of variability observed between radon flux measurement techniques (Hutter and Knutson, 1998; Neznal and Neznal, 2002a), radon flux methodologies should be calibrated, and measurement procedures standardised (e.g. chamber size, closure times), prior to any new flux surveys. Geostatistical methods should be used to design effective sampling programmes for regional-scale surveys (e.g. Oliver and Khayrat, 2001).
There is also a need for more information on $^{222}$Rn emission rates from sources other than soils, such as the oceans and geothermal systems. Although soils are by far the largest source of radon globally (Turekian and Graustien, 2004), these other sources of radon can be important locally, for example, $^{222}$Rn emissions from the ocean are important for understanding variations in atmospheric concentrations at sites with a predominantly oceanic fetch (Taguchi et al., 2002; Zarhorowski et al., 2004a). Recent estimates of the $^{222}$Rn flux from the Southern Ocean made within the fetch of the Cape Grim observatory (Zarhorowski et al., 2004a) are less than previously reported fluxes based on measurements (Wilkening and Clements, 1975), but are in close agreement with estimates based on modelling studies.

More $^{222}$Rn flux measurements based on the integration of atmospheric profiles of $^{222}$Rn measured from towers and aircraft should also be made. Detailed profiles of $^{222}$Rn concentrations are valuable for choosing convection schemes in atmospheric models (e.g. Collins et al., 2002), but reliable data of this type are currently very scarce (Zaucker et al., 1996; Lee and Larsen, 1997; Kritz et al., 1998). Regional $^{222}$Rn flux estimates could also be made by boundary layer budget methods, using $^{222}$Rn concentration data recorded at sites where $^{222}$Rn is routinely monitored at one height (Table 7.1). This could be done by either integrating over distance along particular trajectories (Dörr et al., 1983), or over time during synoptic inversions. Dörr et al. (1983) estimated the regional-scale flux by assuming an average boundary layer height, but more accurate estimates could be obtained by precisely determining the boundary layer depth, for example, by using radiosondes, or acoustic sounding; however, these methods are expensive. Alternative options for obtaining the boundary layer height are modeling based on measured atmospheric parameters, or even using the diurnal variation in the $^{222}$Rn concentration data itself. Kataoka et al. (1998) estimated the depth of the convective mixed layer in this way, and found that estimates were in approximate agreement with depths obtained using the surface sensible heat flux and low-level
sondes. Similarly, Sesena et al. (2003) found that the variation between minimum $^{222}$Rn concentration in the afternoon and the maximum the following morning to be a good indicator of the height of the nocturnal boundary layer. However, most monitoring networks will measure at too high a level to apply this approach (above the nocturnal boundary layer).

Until new $^{222}$Rn flux data and improved data on the parameters required for modelling $^{222}$Rn emissions become available, efforts should be made to improve the spatial and temporal description in emissions on the regional and global scales by means of the currently available data. Current flux maps and models could be improved upon, and need to be tested in more models. For example, there are now new global datasets for variables such as soil moisture and soil temperature that may well improve predictions by the Schery and Wasiolek (1998) model. Both the Schery and Wasiolek (1998) flux map and the $^{222}$Rn source term based on the decreasing trend in emissions in the Northern Hemisphere (Chapter 5/Conen and Robertson, 2002/Appendix A) should be tested in more models. The comparison of the 'northwards-decreasing' $^{222}$Rn source term to the generally-assumed uniform 1 atom cm$^{-2}$ s$^{-1}$ source term carried out as part of this research (Chapter 7/Robertson et al., 2004/Appendix B) indicates that the northwards-decreasing source term is a more realistic representation of reality, but also that the decrease in emissions may only start around 50°N, rather than at 30°N (as indicated by large-scale estimates). The map of Schery and Wasiolek (1998) has also been tested in some models (Schery, 2004), but no quantitative evaluation of this map using $^{222}$Rn data from all the monitoring stations appears to have been carried out. $^{222}$Rn fluxes predicted by this map for higher latitudes in the Northern Hemisphere are much larger than suggested by the large-scale indirect measurements (Conen and Robertson, 2002/Appendix A), thus, it would also be interesting to test a combination of the Schery and Wasiolek (1998) map and the northwards-decreasing source term. The relevance of including $^{222}$Rn emissions from the oceans, and seasonality in emissions should also be
investigated. Although seasonal variations in emissions does not appear to be important for sites with a predominantly oceanic fetch (Robertson et al., 2003/Appendix C; Zahorowski et al., 2004a), they may be important at some continental sites, especially those sites where there is a large amplitude in the seasonal cycle due to changes in water table depth. On the regional scale, the possibility of using routine gamma dose rate measurements made by the national monitoring networks which exist in many countries for the purpose of detecting nuclear accidents should be investigated in more detail (§5.4.2). Although the spatial variability of other gamma-emitting radionuclides is clearly a limitation of this approach (i.e. the relative contribution of $^{40}$K, and $^{238}$U and $^{232}$Th series nuclides to the gamma dose rate is spatially variable), Conen (2004) has demonstrated, using Germany as an example, that this approach has the potential to provide a fast and relatively inexpensive method of providing a description of the spatial pattern in $^{222}$Rn emissions for large areas of the world. This is especially true for regions where the network is relatively dense, or at least dense enough to permit kriging. As temporal variations in the gamma dose rate are largely controlled by atmospheric mixing, it seems unlikely that it will be possible to model the temporal variation in $^{222}$Rn emissions in this way (§5.4.2), but, where necessary, a temporal description of $^{222}$Rn emissions could be added to $^{222}$Rn emissions maps by adding an algorithm based on $^{222}$Rn flux measurements. Where data on the $^{226}$Ra content of the soil are available, $^{222}$Rn emissions maps should also be produced on the basis of observed correlations between $^{222}$Rn flux and the $^{226}$Ra content of the soil, as, given the strong correlation observed between $^{222}$Rn flux and the $^{226}$Ra content of the soil (§5.3.2), it is possible that soil $^{226}$Ra content may provide a more accurate description than gamma dose rate, or any other methods.
8.5 Further research

The main topics of research arising directly from this work which require further investigation are:

1. The effects of freezing of the soil and snow cover on $^{222}\text{Rn}$ and $^{220}\text{Rn}$ emissions. More studies of the effects of snow cover and soil freezing are needed to confirm the findings of this research and those of a small number of other studies. In the case of soil freezing, studies should also be carried out on soils affected by permafrost, as, due to the presence of frozen ice layer and lenses in the soil, these are likely to produce very different and more variable results. Studies in permafrost regions could also further investigate the possibility of using $^{222}\text{Rn}$ soil gas concentrations as an indicator of permafrost distribution (Sellmann and Delaney, 1990). Studies of the effects of snow cover should investigate the difference between fresh and dry snow compared to wet or old snow cover, which has been subject to thawing and freezing.

2. The diurnal variation in radon emissions. Studies need to be carried out to identify what factors or processes are responsible for diurnal variations in $^{222}\text{Rn}$ emissions. To investigate the importance of atmospheric pressure variations, measurements should be carried out over a range of soils of different porosity, and during turbulent and stable atmospheric conditions. The influence of evapotranspiration should be investigated by carrying out measurements at sites with different evapotranspiration characteristics e.g. grassland vs forest.

3. Testing of global source terms in models. Along with the Schery and Wasiolek (1998) model and other modifications of the 1 atom cm$^{-2}$ s$^{-1}$, such as including emissions from the ocean and seasonality in $^{222}\text{Rn}$ emissions, the 'northwards-decreasing' $^{222}\text{Rn}$ source term needs to be tested in more models.


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Appendix A

Latitudinal distribution of radon-222 flux from continents

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ABSTRACT

Global atmospheric transport models are frequently tested by using $^{222}{\text{Rn}}$ as a tracer. Generally this tracer is assumed to be emitted at a uniform rate ($1 \text{ atom cm}^{-2} \text{s}^{-1}$) from all ice-free land surfaces. The analysis of published data suggests a strong decrease from 30°N northwards to 0.2 atom cm$^{-2}$ s$^{-1}$ at 70°N. This could be a result of increasing water tables and proportions of organic soils as indicated by larger proportions of wetlands in northern latitudes.

1. Introduction

The natural radioactive noble gas $^{222}{\text{Rn}}$ is produced by the decay of $^{226}{\text{Ra}}$, a trace element present in all mineral soils. Its emission from ice-free land surfaces is assumed to be relatively uniform. Ice cover inhibits its emission. Oceans, where $^{226}{\text{Ra}}$ is in solution, emit about two orders of magnitude less $^{222}{\text{Rn}}$ than continents. This source distribution and its short half-life ($t_{1/2} = 3.82 \text{ d}$) make $^{222}{\text{Rn}}$ a useful tracer in atmospheric transport studies, an application first proposed by Israel (1951). It is often used in validating global atmospheric transport models (Genthon and Armengaud, 1995; Li and Chang, 1996; Jacob et al., 1997; Stockwell et al., 1998; Dentener et al., 1999; Stockwell and Chipperfield, 1999; Rasch et al., 2000). For this purpose, its large-scale emission rate needs to be known.

By inverse modelling of longitudinal variations in $^{210}\text{Pb}$ flux in the northern (15–55°N) and southern (15–55°S) hemispheres, Turekian et al. (1977) estimated $^{222}{\text{Rn}}$ flux from continents to be $1.2 \text{ atom cm}^{-2} \text{s}^{-1}$. Later, Lambert et al. (1982) used a global inventory of $^{222}{\text{Rn}}$ and its daughter products based on 20 yr of measurements and derived an average $^{222}{\text{Rn}}$ flux of $0.72 \text{ atom cm}^{-2} \text{s}^{-1}$.

In model validations, $^{222}{\text{Rn}}$ flux is generally assumed to be spatially uniform and around $1 \text{ atom cm}^{-2} \text{s}^{-1}$. However, Lee and Feichter (1995) concluded that a non-uniform distribution of the emission rate of $^{222}{\text{Rn}}$ over land would improve predictions of global transport and deposition of $^{210}\text{Pb}$. They demonstrated this by comparing calculations using a constant emission rate with calculations using a simple distribution of latitudinal changes in the emission rates. A similar assumption was made in a comparison of scavenging and deposition processes in global models at the WCRP Cambridge Workshop 1995 (Rasch et al., 2000).

We use this empirical indication of $^{222}{\text{Rn}}$ flux changing with latitude as a hypothesis in re-assessing published data and in evaluating possible implications of own flux measurements on different soils in northern Britain.

2. Radon-222 flux measurements and estimates

2.1. Direct $^{222}{\text{Rn}}$ flux measurements

Radon-222 flux can be directly measured by accumulator methods. In principle, they involve
the interception of gas flux between soil and the atmosphere by an inverted box (chamber) placed onto the soil surface. In a closed, or static system, this results in a usually linear increase in gas concentrations within the chamber. Flux is calculated from the observed concentration change over time, the average chamber height and the gas density. In an open, or dynamic system, outside air is continuously flushed through the chamber and concentration differences between incoming and outgoing air are measured. Flux is then a function of this concentration difference between in-flowing and out-flowing air, flow rate, chamber area, and gas density. Reviews of direct measurements of $^{222}$Rn flux can be found in Wilkening et al. (1975) and Turekian et al. (1977). They generally show a large variability among different sites and between seasons. Apart from genuine differences in flux, differences in measurement techniques and apparatus also need to be considered. Flutter and Knutson (1998) found a coefficient of variation of 34% for $^{222}$Rn flux measured at the same location by nine different groups.

Since the last review of which we are aware [Turekian et al. (1977)], many more $^{222}$Rn flux measurements from natural soils have been reported (Table 1). Some of this work specifically focused on the determination of $^{222}$Rn flux from larger areas (e.g. Schery et al., 1989; Whittlestone et al., 1998; Nielson et al., 1996). In some of the other studies, $^{222}$Rn flux measurements were limited to a few locations, or part of an experiment with a different focus. These directly measured fluxes show a similar average flux and variability, as previous flux measurements reported. Given the large variability of the data, there is no clear indication of a trend in $^{222}$Rn flux across latitudes.

2.2. Indirect $^{222}$Rn flux estimates

Indirect flux estimates from measurement of atmospheric $^{222}$Rn profiles and the assumption of steady-state conditions between flux and decay have the advantage of integrating over large areas. Unlike direct measurements, they are not subject to small-scale variations in soil properties. However, for a near equilibrium between flux and decay to establish, air masses have to be in contact with a land surface for over a week. Indirect flux estimates of this kind have been made in the mid-latitudes of the northern hemisphere in France (Servant, 1964, cited in Wilkening et al., 1975), the former USSR (Kirichenko, 1990) and in the USA (Anderson and Larson, 1974; Wilkening et al., 1975). When plotted against latitude, they exhibit a decreasing trend with increasing latitude (Fig. 1). The same data plotted against longitude did not exhibit any trend.

Indirect estimation of $^{222}$Rn flux is also possible from measurements of $^{210}$Pb flux. Decay of $^{222}$Rn in the atmosphere results in the formation of $^{210}$Pb ($t_{1/2} = 22.3$ yr) which attaches to submicron-sized aerosols. The mean residence time of these particles in the atmosphere is around 6.5 d (Lambert et al., 1982) before they are scavenged by precipitation or deposited dry. While emission of the parent element $^{222}$Rn is almost exclusively from continents, the daughter product $^{210}$Pb is deposited on continents and oceans likewise. In order to estimate the average $^{222}$Rn flux from continents in a certain latitudinal band, we might therefore divide the average $^{210}$Pb deposition flux by the proportion of ice free continental area within this band.

Such an estimate is based on several assumptions. Firstly, that the number of $^{210}$Pb atoms deposited is equal to the number of $^{222}$Rn atoms emitted. This is very likely to be true because of the principal of continuity (Turekian et al., 1977) and the absence of any significant other sources of $^{210}$Pb (Lambert et al., 1982). Secondly, that within a certain latitudinal band there is no bias in the allocation of $^{210}$Pb measurement sites to areas with particularly low or high $^{210}$Pb deposition fluxes. This seems correct for the latitudes north of 30°N, where $^{210}$Pb flux has been measured at a large number of sites in America, Europe and Japan, including continental, coastal and maritime sites. However, south of 30°N, $^{210}$Pb flux measurements are more sparse and are concentrated in a few regions, rendering this assumption less likely. The third assumption is that transfer of air masses from one latitudinal band into another is negligible. This is supported by the prevailing atmospheric circulation being either from west to east (30–60°N), or from east to west (10–30°S). Nevertheless, some loss or entrainment of $^{210}$Pb from one latitudinal band into another is possible and might lead to an under- or over-estimation of $^{222}$Rn flux.

To estimate $^{222}$Rn flux based on this approach we can use the average values of $^{210}$Pb flux for
LATITUDINAL DISTRIBUTION OF $^{222}\text{Rn}$ FLUX

Table 1. Reported $^{222}\text{Rn}$ flux from natural soils since review by Turekian et al. (1977)

<table>
<thead>
<tr>
<th>Country</th>
<th>Latitude</th>
<th>$^{222}\text{Rn}$ flux (atom cm$^{-2}$ s$^{-1}$)</th>
<th>No. of samples</th>
<th>No. of different sites sampled</th>
<th>Temporal scale</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>54°N</td>
<td>0.54</td>
<td>8</td>
<td>2</td>
<td>Jul + Aug</td>
<td>Usler et al. (1994)</td>
</tr>
<tr>
<td>Canada</td>
<td>50°N</td>
<td>0.33</td>
<td>51</td>
<td>51</td>
<td>Aug + Sept</td>
<td>Kuhlmann et al. (1998)</td>
</tr>
<tr>
<td>Germany</td>
<td>50°N</td>
<td>0.08-0.19</td>
<td>11</td>
<td>6</td>
<td></td>
<td>Keller and Schütz (1988)</td>
</tr>
<tr>
<td>Germany</td>
<td>49°N</td>
<td>0.88</td>
<td>&gt;1000</td>
<td>5</td>
<td>Annual average</td>
<td>Dör et al. (1983)</td>
</tr>
<tr>
<td>Germany</td>
<td>49°N</td>
<td>0.75</td>
<td></td>
<td></td>
<td>8 year average</td>
<td>Schüller (1996), cited in Levin et al. (1999)</td>
</tr>
<tr>
<td>Romania</td>
<td>46°N</td>
<td>0.95</td>
<td>9</td>
<td>3</td>
<td>Oct, Nov + Mar</td>
<td>Coma et al. (1996)</td>
</tr>
<tr>
<td>Spain</td>
<td>37°N</td>
<td>0.60</td>
<td>235</td>
<td>4</td>
<td>Jan, Feb, Jun + Oct</td>
<td>Dueñas et al. (1997)</td>
</tr>
<tr>
<td>Japan</td>
<td>36°N</td>
<td>0.48</td>
<td>9</td>
<td>2</td>
<td>Jul-Oct</td>
<td>Uchida et al. (1997)</td>
</tr>
<tr>
<td>Japan</td>
<td>35°N</td>
<td>0.48</td>
<td></td>
<td>13</td>
<td>Annual average</td>
<td>Tojo (1989); cited in Motriuzi et al. (1996)</td>
</tr>
<tr>
<td>Japan</td>
<td>35°N</td>
<td>0.41</td>
<td></td>
<td></td>
<td>Oct, Dec + Jan</td>
<td>Koorashi et al. (2000)</td>
</tr>
<tr>
<td>USA</td>
<td>26-31°N</td>
<td>0.70</td>
<td>882</td>
<td>882</td>
<td>Apr + Jun</td>
<td>Nielson et al. (1996)</td>
</tr>
<tr>
<td>India</td>
<td>15°N</td>
<td>1.43</td>
<td>13</td>
<td></td>
<td></td>
<td>Samshakrappa et al. (1996)</td>
</tr>
<tr>
<td>Brazil</td>
<td>3°S</td>
<td>0.38</td>
<td>20</td>
<td>8</td>
<td>April + May</td>
<td>Trumbore et al. (1996)</td>
</tr>
<tr>
<td>Australia</td>
<td>11-39°S</td>
<td>1.05</td>
<td></td>
<td>Seasonally adjusted annual average</td>
<td></td>
<td>Schery et al. (1989)</td>
</tr>
<tr>
<td>Tasmania</td>
<td>41-44°S</td>
<td>1.20</td>
<td>78</td>
<td>120</td>
<td>Jun + Jul</td>
<td>Whittlestone et al. (1998)</td>
</tr>
</tbody>
</table>

* Data not given in reference
* Continuous measurement.

Only the arithmetic mean is indicated for locations where more than one value was given in the same reference (i.e. measurements at different times or different soils).

Fig. 1. Indirect measurements of $^{222}\text{Rn}$ flux in the mid-latitudes of the northern hemisphere. The decreasing trend with increasing latitude is supported by estimates derived from $^{210}\text{Pb}$ deposition flux (horizontal bars indicate the latitudes over which this flux is integrated). ■, Servant (1964); ●, Kirichenko (1970); ▲, Anderson and Larson (1974); △, Wilkening et al. (1975); ○, derived from $^{210}\text{Pb}$ fluxes in Preiss et al. (1996).

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different latitudinal bands as reported in Preiss et al. (1996). This gives us $^{222}\text{Rn}$ flux values of 0.75 atom cm$^{-2}$ s$^{-1}$ for the latitudinal band 30-60°N, and 0.18 atom cm$^{-2}$ s$^{-1}$ for 60-80°N. These values will probably only have a small error because the discussed assumptions are most likely for these two latitudinal bands. They support the trend indicated by the atmospheric $^{222}\text{Rn}$ profiles in the same latitudes (Fig. 1). Consequently, the $^{222}\text{Rn}$ flux distribution based on indirect estimates suggests a linear decrease from 1 atom cm$^{-2}$ s$^{-1}$ at 30°N to 0.2 atom cm$^{-2}$ s$^{-1}$ at 70°N.

Radon-$^{222}\text{Rn}$ flux derived from $^{210}\text{Pb}$ deposition flux in the 10-30°N band gives a value of 1.8 atom cm$^{-2}$ s$^{-1}$. This is certainly an overestimate resulting from the concentration of $^{210}\text{Pb}$ flux measurements in monsoon-influenced regions, where fluxes are expected to be much larger than in drier regions, such as the Sahara or Arabia (Rasch et al., 2000), from where there are no reported $^{210}\text{Pb}$ flux measurements. Lack of $^{210}\text{Pb}$ flux data from the equatorial regions precludes a
similar estimate between 10°N and 10°S. The
\( ^{210}\text{Pb} \)-based estimate between 10 and 30°S
(0.93 atom cm\(^{-2}\) s\(^{-1}\)) is very similar to the average
of 1.05 atom cm\(^{-2}\) s\(^{-1}\) for the Australian continent
(11–39°S) measured directly by Schery et al.
(1989). However, lack of \(^{210}\text{Pb} \) flux values from
southern Africa and South America reduces the
confidence, we might put into the \(^{210}\text{Pb} \)-based
estimate for these latitudes. For the more southern
latitudes (30–50°S), the \(^{210}\text{Pb} \)-derived \(^{222}\text{Rn} \)
flux seems again unreasonably high (2.8
atom cm\(^{-2}\) s\(^{-1}\)). Entrainment of small quantities
of \(^{210}\text{Pb} \) into these latitudes from further north
could result in a large over-estimate because of
the small proportion of ice free continental area
(0.06) in these latitudes.

3. Possible relations between latitude and
\(^{222}\text{Rn} \) flux

While the evidence for decreasing \(^{222}\text{Rn} \) flux in
northern latitudes is strong, it remains open which

Fig. 2. (a) Radon-222 flux from February to June 2001 at three sites in Britain differing in the proportion of the
humic layer in the soil profile. As (b) water tables decrease, (c) fluxes increase relative to respective site average.

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factors or processes are causing this. One possibility could be wetter, and more organic, soils and shallower water tables in increasingly northern latitudes. Such a trend is indicated in the increasing proportion of peat bogs and other wetlands per unit land area with increasing latitude in the northern hemisphere (Stillwell-Soller et al., 1995). Compared to mineral soils, organic soils or peat have orders of magnitude lower concentrations of $^{226}$Ra. This would result in reduced $^{222}$Rn fluxes from humic soils, since $^{222}$Rn flux is proportional to soil $^{226}$Ra content, if all other factors are equal. Further, shallow water tables in wetlands reduce the thickness of the soil profile from which $^{222}$Rn can escape into air spaces and diffuse into the atmosphere, as $^{222}$Rn produced below the water table is unlikely to enter air space before its decay. Higher soil moisture contents associated with shallower water tables further reduces soil gas diffusivity and $^{222}$Rn flux. This results in increased retention times of $^{222}$Rn within the soil pore space and a larger proportion of it decaying before escape into the atmosphere (Dörre and Münich, 1990).

To investigate these assumptions, we made direct measurements in the north of Britain at sites between 55 and 57°N contrasting in the thickness of their humic layer and at times of different water table depth. Volumetric soil water content was on average around 35% and rarely below 25%. The soil was never frozen when the measurements were made. The underlying material at all sites is of sedimentary origin. Fluxes were measured with four replicate closed chambers and samples (1 litre) were analysed in an ionisation chamber. Radon-$^{222}$ flux decreased in the order: mineral soil, no humic layer > mineral soil with 15 cm humic top layer > humic soil (peat) (Fig. 2). We also found that fluxes increase with decreasing water table. It is unlikely that temperature had a significant effect on the observed changes in $^{222}$Rn flux, since $^{222}$Rn emanation and transport processes in soils are only very weakly affected by temperature, if at all (Schery et al., 1989; Nazaroff, 1992). These results support the assumption that an increasing proportion of more organic soils and water tables closer to the soil surface would decrease $^{222}$Rn flux in northern latitudes.

Another possible cause for decreased $^{222}$Rn flux with increasing latitudes could be differences in $^{238}$U content in mineral soils. Evidence pointing in this direction has been found in China, where concentrations of $^{238}$U (a source of $^{226}$Ra) in soils have been found to decrease from south to north (Xu et al., 1993). This trend has been attributed to the pattern of geochemical weathering and the effect of leaching on soil development.

4. Proposed $^{222}$Rn flux distribution across latitudes

Starting from the assumption of a uniform $^{222}$Rn flux of 1 atom cm$^{-2}$ s$^{-1}$ from ice-free continental areas, we might now apply the constraint of linearly decreasing $^{222}$Rn flux with increasing latitude from 1 atom cm$^{-2}$ s$^{-1}$ at 30°N to 0.2 atom cm$^{-2}$ s$^{-1}$ at 70°N. From 30°N into the equatorial region, measurements are sparse, but reported direct flux measurements are generally in the same range as at 30°N (Table 1), supporting the assumption of 1 atom cm$^{-2}$ s$^{-1}$ for these latitudes. The area-weighted average for the northern hemisphere, based on this distribution would be 0.7 atom cm$^{-2}$ s$^{-1}$, which is in accordance with the estimate of 0.72 atom cm$^{-2}$ s$^{-1}$ by Lambert et al. (1982). Constraining flux distribution for the southern hemisphere is limited by low data density. Nevertheless, directly measured fluxes in Australia agree well with an indirectly derived $^{222}$Rn flux estimate for the 10-30°S latitudinal band and support the general assumption of 1 atom cm$^{-2}$ s$^{-1}$ for these latitudes. The southern-most reported flux measurements are from Tasmania (41-44°S) and are in a similar range.

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Appendix B

Test of a northwards-decreasing 222Rn source term by comparison of modelled and observed atmospheric 222Rn concentrations

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Abstract

Model-predicted atmospheric concentrations of 222Rn based on two different 222Rn source terms have been compared with observations in the lower troposphere. One simulation used a globally uniform 222Rn source term from ice-free land surfaces of 1 atom cm⁻² s⁻¹; the other assumed a northwards-decreasing source term (linear decrease from 1 atom cm⁻² s⁻¹ at 30°N to 0.2 atom cm⁻² s⁻¹ at 70°N). Zero emissions were assigned to oceans. The northwards-decreasing source term improved predictions at four out of six stations north of 50°N, reducing the mean prediction/observation ratio from 2.8 to 0.87. In the latitudinal band between 30°N and 50°N, the northwards-decreasing source term resulted in systematic under-prediction of atmospheric 222Rn, whereas the uniform source term provided predictions close to observations. Predictions based on the northwards-decreasing source term were significantly (p < 0.01) better than those based on the uniform source term for an averaged vertical 222Rn profile around 44°N, but were not for one around 38°N. The results indicate that a northwards-decreasing source term could be a more realistic representation of actual 222Rn emissions than a uniform 1 atom cm⁻² s⁻¹ source term. However, the decrease in 222Rn source strength with increasing latitude might not begin at 30°N but somewhat further north. This hypothesis should be investigated through model-independent means.

1. Introduction

The radioactive noble gas 222Rn (half-life = 3.82 d) is frequently used in the evaluation and intercomparison of atmospheric transport models (Brost and Chatfield, 1989; Feichtér and Creeden 1996; Genthon and Arnéngaud, 1995; Jacob et al., 1996; Jacob et al., 1997; Stevenson et al., 1998; Dentener et al., 1999 and references therein). In an attempt to improve model predictions of atmospheric 222Rn concentrations, some workers have modified this uniform 222Rn flux distribution so as to take into account some of the variability in 222Rn emissions. For example, Lee and Feichtér (1995) assumed a reduced source strength of 0.005 atom cm⁻² s⁻¹ between 60 and 70°N, to account for apparent snow cover and soil freezing effects, and found that this improved model predictions of 210Pb deposition rates. This source distribution was also used in the 1993 World Climate Research Program (WCRP) sponsored intercomparison of global atmospheric transport models (Jacob et al., 1997), and a similar modification (0.5 atom cm⁻² s⁻¹ between 60 and 70°N) was made in the 1995 WCRP workshop (Rasch et al., 2000). Other modifications of the 222Rn source term which have been used include: accounting for a small oceanic flux (Heimann et al., 1990; Taguchi et al., 2002); taking into account variations in emissions due to soil texture (Dentener et al., 1999; Chevillard et al., 2002) and snow cover (Dentener et al., 1999); and increased emissions from Southeast Asia (Dentener et al., 1999; Taguchi et al., 2002). Some have also tried to improve 222Rn predictions by taking into account temporal changes in 222Rn flux (Jacob and Prather, 1990; Genthon and Arnéngaud, 1995; Lin et al., 1996). However, where any effects of these spatial and temporal modifications on predicted concentrations has been found, they have generally not been quantified.

Recently, a more far-reaching modification in the global 222Rn flux term has been proposed by Conen and Robertson (2002).
It is based on an empirical relationship between 222Rn emissions and latitude which has been derived from published indirect 222Rn flux measurements and estimates calculated from 210Po fluxes. With this distribution of emissions, the 222Rn flux is 1 atom \( \text{cm}^{-2} \text{s}^{-1} \) between 60°S and 30°N, and from thereon decreases linearly to 0.2 atom \( \text{cm}^{-2} \text{s}^{-1} \) at 70°N. 222Rn emissions are expected to decrease with increasing latitude in the Northern Hemisphere as a result of the increasing proportion of wetlands and organic soils (Stillwell-Soifer et al., 1995; Conen and Robinson, 2002). Only 222Rn produced in aerated surface layers of the soil is likely to escape to the atmosphere before its decay. Regional gradients in soil 226Ra content caused by geochemical weathering patterns may also contribute to this trend, as appears to be the case in China where concentrations of 222Ra precursors decrease from south to north (Xu et al., 1993; Sun et al., 2004). South of 60°S and north of 70°N, 222Rn emissions are assumed to be zero. However, small fluxes (0.077 atom \( \text{cm}^{-2} \text{s}^{-1} \)) have been reported at 62°S during the brief Antarctic summer (Evangelista and Pereira, 2002). In this paper, we present the results of a study to find if this new source term improves predictions of 222Rn compared with use of the uniform 222Ra source term of 1 atom \( \text{cm}^{-2} \text{s}^{-1} \) between 60°S and 70°N. The observational data used were long-term average 222Rn concentrations for 23 ground-based stations and two averaged vertical profiles. The model used was STOCHEM-EaJ (Stevenson et al., 2003), a new version of the UK Met Office global chemistry-transport-model (CTM), first described in Collins et al. (1997).

2. Observations, model and simulations

2.1. Surface observations

The data used for surface comparisons were published monthly mean 222Rn concentrations available for 22 sites located at different latitudes, and data for the Cape Grim baseline air pollution station (W. Zaborowski, personal communication). The locations of these stations are shown in Fig. 1a, and details of each site are summarized in Table 1. Station locations range in latitude from 68°N (Pallas, Finland) to the South Pole, with 13 stations north of 30°N and 10 stations south of 30°N. Long-term means of surface 222Rn concentrations were calculated from reported monthly means, except for Mauna Loa and Bermuda, where published values were monthly medians. For Pallas and New York City, where 222Rn concentrations have been published for more than...
one height, we chose the greatest available height as the most representative of the concentrations in the lowest layer in our model. For Pallas this was Sammaltuitturi station, which is on a hillside 565 m above sea level (asl) and around 200 m above the surrounding area, and for New York City this was 260 m above street level. By averaging over the longest timescale available, much of the temporal variation in $^{222}$Rn concentrations is eliminated (Robé et al., 1992). Thus, comparisons with predictions become less subject to the ability of the model to faithfully reproduce temporal variations in $^{222}$Rn concentrations, and a larger proportion of any discrepancy between prediction and observations becomes attributable to the differences between the actual and assumed $^{222}$Rn source terms or systematic deficiencies in the model. One measure of the discrepancy between prediction and observation we have used is the average of prediction/observation ratios, the other is the root-mean-square error of prediction relative to observation.

2.2. Vertical profile observations

The vertical profile data used were those published in Kritz et al. (1998) and Zaucker et al. (1996). These data are the most recent, reliable and detailed $^{222}$Rn profile data available. The data in Kritz et al. (1998) were collected in the vicinity of Moffet Field, California, USA (-38°N, 122°W). Measurements were made during the period from 3 June to 16 August 1994 and consisted of 11 flights up to 11.5 km altitude. The data in Zaucker et al. (1996) were collected over Nova Scotia, New Brunswick, and the western North Atlantic Ocean (-44°N, 64°W), with flights originating from Halifax. These measurements were made between the 16 and 31 August 1993 as part of the North Atlantic Regional Experiment (NARE) campaign, and consisted of nine flights up to 5500 m. For each data set, an average $^{222}$Rn profile was compiled from the separate flights by averaging measured values over 1000 m intervals, and 2000 m intervals for greater altitudes. No interpolation was made. The measurements were compared with the model layers corresponding to the same height intervals.

2.3. Model

STOCHEM-Ed is a new version of the UK Met Office 3-D Lagrangian CTM STOCHEM (Collins et al., 2000, 2002, 2003), developed at the University of Edinburgh. STOCHEM-Ed is closely coupled to the Unified Model (UM) general circulation model (GCM) (Johns et al., 1997), from which it is receiving meteorological fields every 3 h. Earlier versions of STOCHEM have taken part in a number of intercomparisons regarding transport and chemistry, including the 1995 WCRP workshop (Rasch et al., 2000). In all of these studies the model was typically found to perform well within the
range of other current models. Thus, we would expect the results of this study to also be valid for other global atmospheric models, although this should be tested.

STOCHEM-Ed uses a Lagrangian transport scheme, dividing the atmosphere into 50 000 air parcels of equal mass. These parcels are advected by winds from the GCM with a fourth-order Runge-Kutta algorithm, using linear horizontal interpolation and cubic vertical interpolation, and adding a small random walk component to simulate turbulent diffusive mixing.

The parcels maintain approximately equal global distribution with time. Convective mixing is implemented by fully mixing a fraction of the parcels beneath a convective cloud top. The precipitation rate and fractional cloud cover determine the amount mixed (Stevenson et al., 1998). Interparcel mixing occurs between parcels occupying the same grid box after each 1 h advection step. Turbulent mixing in the boundary layer is achieved by randomly reassigning the vertical coordinates of air parcels over the depth of the layer. The grid used for mixing is 5° × 5°, with 22 vertical hybrid (α) levels (six levels with Δα = 0.1 between α = 1.0 and α = 0.4, 15 levels with Δα = 0.025 between α = 0.4 and α = 0.025, and a top level between α = 0.025 and α = 0.0003). Hybrid coordinates are explained further in Collins et al. (1997), but can be considered as approximately equal to pressure divided by surface pressure. The vertical resolution of the surface boundary layer in STOCHEd is quite coarse, with the lowest six levels being approximately 100 hPa thick (≈1 km). The boundary layer is therefore typically represented by only one or two levels. The top level is in the stratosphere, well above the highest level of interest for 222Rn (approximately stratosphere levels). The driving GCM has a more highly resolved boundary layer, which is represented by six different levels. Surface tracer gas emissions are added to air parcels within the boundary layer above their sources. Gribed emission distributions with a horizontal resolution of 5° × 5° are used. When several air parcels occupy the boundary layer for the grid square, emissions are divided equally between them. If no air parcels are present, for example when the boundary layer is very shallow, emissions are stored until the next time step, ensuring mass conservation. A more detailed description of STOCHEd can be found in Stevenson et al., 2003.

2.4. Simulations

For each 222Rn source term one 15-month simulation was carried out, the first 3 months of which were discarded as spin-up time. The meteorological driver (UM) was configured as an atmosphere-only GCM, with a resolution of 3.75° longitude by 2.5° latitude and with 58 vertical levels between the surface and 0.1 hPa. Recent climatologies of sea-surface temperatures and stratospheric ozone were used to drive the GCM. The modelled values of 222Rn for each station are linearly interpolated from the four surrounding grid boxes, where the values for a grid box are taken to be representative of its central latitude and longitude.

The grid boxes are illustrated in Fig. 1a. For all stations except Mauna Loa (3400 m asl) and Jungfraujoch (3580 m asl) the 222Rn concentrations used in the comparison were for the lowest model layer. For Mauna Loa this was the second layer. At Jungfraujoch, strong diurnal variations in 222Rn with maxima during late afternoon in summer, and the absence of variations in winter, indicate the influence of the convective boundary layer in summer and exposure to the free troposphere in winter (Gäggeler et al., 1995). Thus, for Jungfraujoch we used model layer 2 (centered 1200 m above the local ground surface) for June to September, and model layer 3 (centered 2000 m above the local ground surface) the rest of the year.

3. Results and discussion

The assumption of a decreasing 222Rn source strength north of 30°N only notably affected predicted 222Rn concentrations in the Northern Hemisphere (Table 2), as we would expect given the mean atmospheric (or e-folding) lifetime of 222Rn of 5.5 d. Differences in atmospheric 222Rn concentrations between the two simulations were largest in the surface layer polewards of 40°N, with peak differences towards the centres of large land masses (Canada and Siberia). In relative terms, the northwards-decreasing source term resulted in a reduction of more than 70% in surface layer concentrations northwards of 60°N (Fig. 1b). This difference between the two simulations decreased steadily with decreasing latitude, and at 30°N was less than 10% over the continents and less than 30% over the centre of the oceans.

In this study, the approach taken to comparing predictions with observations is somewhat different from that of previous studies. For each site, predictions and observations have been averaged over the longest timescale available, without taking into account variations over shorter timescales (e.g. Dentener et al., 1995; Tsiguschi et al., 2002). In this way, the influence of random errors in the comparison, for both observations and predictions, has been reduced. We did not attempt to judge the quality of the measurements reported, assuming that instrumental bias is distributed randomly among the 23 stations and averages zero. Using the largest number of stations possible should then result in the smallest bias in the overall judgement. If the model is a perfect representation of reality and bias among the stations is distributed as assumed, we would expect prediction and observation to converge towards the same value with increasing averaging time and increasing number of stations included in the comparison. If this is not the case, systematic deficiencies of the model, the observations or both could be responsible. However, currently, the most important systematic uncertainty in matching predictions with observations seems to be uncertainties in 222Rn emissions (Schery and Wasiolek, 1998; Chevillard et al., 2002); thus, the similarity of predicted and observed long-term averages at a large number of stations should be an indication of the accuracy of the 222Rn source term employed.

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Table 2. Observed and predicted long-term $^{222}$Rn concentrations (in Bq m$^{-3}$) for two different $^{222}$Rn source term assumptions

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Station</th>
<th>Observation</th>
<th>Uniform</th>
<th>Northwards-decreasing</th>
<th>Prediction</th>
<th>Prediction/Observation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.0°N</td>
<td>Pallan</td>
<td>1.22</td>
<td>1.54</td>
<td>0.43</td>
<td>1.26</td>
<td>0.36</td>
</tr>
<tr>
<td>65.6°N</td>
<td>Wales</td>
<td>0.74</td>
<td>0.98</td>
<td>0.25</td>
<td>1.33</td>
<td>0.33</td>
</tr>
<tr>
<td>57.8°N</td>
<td>Kodiak</td>
<td>0.36</td>
<td>1.94</td>
<td>0.51</td>
<td>3.33</td>
<td>1.39</td>
</tr>
<tr>
<td>56.3°N</td>
<td>Fyodorovskoye</td>
<td>1.45</td>
<td>4.62</td>
<td>1.44</td>
<td>3.19</td>
<td>1.00</td>
</tr>
<tr>
<td>54.4°N</td>
<td>Zingst</td>
<td>1.33</td>
<td>3.27</td>
<td>1.24</td>
<td>2.46</td>
<td>0.93</td>
</tr>
<tr>
<td>53.3°N</td>
<td>Mace Head</td>
<td>0.44</td>
<td>1.44</td>
<td>0.33</td>
<td>3.26</td>
<td>1.20</td>
</tr>
<tr>
<td>49.4°N</td>
<td>Heidelberg</td>
<td>4.13</td>
<td>3.31</td>
<td>1.24</td>
<td>3.02</td>
<td>0.35</td>
</tr>
<tr>
<td>47.9°N</td>
<td>Schauinsland</td>
<td>2.02</td>
<td>3.17</td>
<td>1.48</td>
<td>3.77</td>
<td>0.73</td>
</tr>
<tr>
<td>46.8°N</td>
<td>Jungfraujoch</td>
<td>0.58</td>
<td>0.81</td>
<td>0.42</td>
<td>1.40</td>
<td>0.73</td>
</tr>
<tr>
<td>45.7°N</td>
<td>New York City</td>
<td>3.40</td>
<td>3.25</td>
<td>1.78</td>
<td>0.95</td>
<td>0.52</td>
</tr>
<tr>
<td>40.0°N</td>
<td>Cincinnati</td>
<td>5.04</td>
<td>3.71</td>
<td>2.23</td>
<td>0.74</td>
<td>0.44</td>
</tr>
<tr>
<td>35.3°N</td>
<td>Yokosuka</td>
<td>2.06</td>
<td>2.12</td>
<td>0.97</td>
<td>1.03</td>
<td>0.47</td>
</tr>
<tr>
<td>32.3°N</td>
<td>Tudor Hill</td>
<td>0.46</td>
<td>0.59</td>
<td>0.36</td>
<td>1.29</td>
<td>0.78</td>
</tr>
<tr>
<td>19.5°N</td>
<td>Maua Loa</td>
<td>0.18</td>
<td>0.11</td>
<td>0.07</td>
<td>0.59</td>
<td>0.40</td>
</tr>
<tr>
<td>12.0°S</td>
<td>Lima</td>
<td>1.15</td>
<td>1.94</td>
<td>1.84</td>
<td>1.69</td>
<td>1.69</td>
</tr>
<tr>
<td>15.7°S</td>
<td>Chacaltaya</td>
<td>1.44</td>
<td>2.64</td>
<td>2.64</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>23.0°S</td>
<td>Rio de Janeiro</td>
<td>1.52</td>
<td>1.28</td>
<td>1.28</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>46.4°S</td>
<td>Cape Grim</td>
<td>0.68</td>
<td>0.59</td>
<td>0.59</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>46.0°S</td>
<td>Crozet Island</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
<td>1.60</td>
<td>1.60</td>
</tr>
<tr>
<td>54.5°S</td>
<td>Macquarie Island</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.94</td>
<td>0.64</td>
</tr>
<tr>
<td>70.6°S</td>
<td>Gough v. Neumayer</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>78.2°S</td>
<td>Little America V</td>
<td>0.10</td>
<td>0.01</td>
<td>0.01</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>90.0°S</td>
<td>South Pole</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.53</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 3. Surface data mean prediction/observation ratios and root-mean-square error of prediction relative to observation (RMSE) for three areas of geographical coverage

<table>
<thead>
<tr>
<th>Geographical coverage</th>
<th>No of stations</th>
<th>Mean prediction/observation ratio</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uniform</td>
<td>Northwards-decreasing</td>
<td></td>
</tr>
<tr>
<td>North of 50°N</td>
<td>6</td>
<td>2.80</td>
<td>0.87</td>
</tr>
<tr>
<td>30°N-50°N</td>
<td>7</td>
<td>1.11</td>
<td>0.58</td>
</tr>
<tr>
<td>South of 30°N</td>
<td>10</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>Global</td>
<td>23</td>
<td>1.49</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>Uniform</td>
<td>Northwards-decreasing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.27</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.31</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.22</td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>

Globally, the northwards-decreasing $^{222}$Rn source term resulted in a mean prediction/observation ratio (0.82) closer to unity than the uniform source term assumption (1.49) (Table 3). Also, the root-mean-square error was smaller (0.49) for the northwards-decreasing source term compared with 1.22 for the uniform source term assumption. However, when we take a more differentiated look, we find that this improvement was mainly due to an improvement in prediction at stations north of 50°N, where predictions were improved at four out of six stations. For stations north of 50°N the uniform source term resulted in an almost three-fold (2.80) overestimation, whereas predictions based on the northwards decreasing source term were relatively close to unity (0.87). Yet, in the latitudinal band between 30°N and 50°N, predictions based on the uniform source term were closer to observations at four out of seven stations and mean prediction/observation ratios were much closer to unity (1.11) than for predictions based on the northwards decreasing source term (0.58). South of 30°N, little difference was found between the two sets of predictions. In both cases, mean prediction/observation ratios were close to unity (0.97; 0.96) and the root-mean-square error was slightly over 0.5. This last result gives some confidence in the model not being particularly biased.
Towards under- or overestimation. Thus, for our comparison of different 222Rn source terms we can suppose that both the better results north of 50°N as well as the underestimate between 30°N and 50°N for the northwards-decreasing source term assumption are likely to be genuine.

Predicted and observed 222Rn concentrations for the two vertical profiles are shown in Fig. 2. Mean 222Rn concentrations were greater for the Nova Scotia/North Atlantic Ocean profile (Zaucker et al., 1996) than for the Californian profile (Kaufman et al., 1998), despite the fact that air samples for the first profile were largely collected over the ocean. However, given the predominantly westerly winds at these latitudes, west coast locations are likely to be more strongly influenced by 222Rn-poor maritime air, and east coast locations more strongly influenced by 222Rn-rich continental air, and thus 222Rn concentrations will tend to be greater on the east coast of the continent. The largest differences in absolute terms between the two sets of predicted concentrations occur in the surface layer, as we would expect. In relative terms, however, the decrease was as large or larger at higher levels. The differences are greater for the Nova Scotia profile than for the California profile because of the higher latitude of this region (Fig. 2). At 44°N (the latitude of the Nova Scotia profile) the northwards-decreasing source term assumes 28% less emission, but only 16% less at 38°N (the latitude of the Californian profile). Mean prediction/observation ratios and the root-mean-square error of prediction relative to observation for each profile are given in Table 4. For the Nova Scotia data there was substantial improvement in model predictions when changing to the northwards-decreasing 222Rn source term, especially at heights above 2000 m. The mean prediction/observation ratio for all height intervals altered from 1.40 to 0.72, and the root-mean-square error of prediction relative to observation was reduced from 0.52 to 0.33. Changing to the northwards-decreasing 222Rn source term shifted the mean prediction/observation ratio away from unity for the California profile, but predictions were improved for the lowest two height intervals. Similar results to this (improved prediction for the Nova Scotia profile but no improvement for the California profile) have been found by Gupta et al. (2004), in a study in which they compared the northwards-decreasing source term with the source term used in the 1993 WCRP workshop (Jacob et al., 1997). As for the results for the surface data, this observation suggests that the northwards-decrease in 222Rn source strength begins somewhat north of 30°N.

### 4. Conclusions

The comparison of observed and predicted 222Rn concentrations lends, in general, support to the assumption of a decrease in 222Rn source strength with increasing latitude in the Northern Hemisphere. Empirical evidence based on indirect 222Rn flux measurements and estimates derived from 226Ra fluxes suggests

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**Table 4. Vertical profile mean prediction/observation ratios and root-mean-square errors of prediction relative to observation (RMSE)**

<table>
<thead>
<tr>
<th>Region</th>
<th>No of height intervals</th>
<th>Uniform Mean prediction/observation ratio</th>
<th>Northwards-decreasing</th>
<th>Root-Mean-Square Error of Prediction relative to Observation (RMSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nova Scotia</td>
<td>6</td>
<td>1.40</td>
<td>0.72</td>
<td>0.52</td>
</tr>
<tr>
<td>California</td>
<td>16</td>
<td>1.04</td>
<td>0.59</td>
<td>0.55</td>
</tr>
</tbody>
</table>

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that fluxes decrease northwards of 50°N. However, the validation of this suggestion through comparison of predicted and observed atmospheric 222Rn concentrations yielded mixed results. While the northwards-decreasing source term substantially improved predictions north of 50°N compared with a uniform source term of 1 atom cm$^{-2}$ s$^{-1}$, it also resulted in a systematic underprediction of 222Rn concentrations in the latitudinal band between 30°N and 50°N, a region where predictions based on the uniform source term were closer to observations. Although this study does not provide a proof of one particular source term, it indicates that the northwards-decreasing source term is a more realistic representation than the generally used uniform 1 atom cm$^{-2}$ s$^{-1}$ source term. It also suggests that this decrease begins somewhere between 30°N and 50°N, rather than at 30°N as indicated by the available flux measurements. Future investigations into 222Rn fluxes should therefore concentrate on these latitudes. Whilst this study suggests a geographical region where further refinement might be necessary, appropriate investigation needs to be made by other means, otherwise the derived source term will not be model-independent and therefore cannot be used in future model validations. Guidance for further improvement of 222Rn parameterisation has recently been worked out in an expert meeting supported by the World Meteorological Organization/GLOBAL Atmosphere Watch (WMO/GAW, 2004). This includes, amongst others, the quest for quality controlled measurements of 222Rn emissions along north–south transects in Europe and North America, and improved knowledge of global surface 222Rn concentrations.

5. Acknowledgments

We are grateful to the Cape Grim baseline air pollution station and to Dr Włodzicka Zaborowski of the Australian Nuclear Science and Technology Organisation for providing atmospheric 222Rn data for Cape Grim. DS thanks the Environment Agency (F4-F02) and the Natural Environmental Research Council (NERC) for fellowship funding (NER/J/S/2000/00840). LR carried out this research whilst in receipt of a NERC PhD studentship.

References


A NORTHWARDS-DECREASING $^{222}\text{Rn}$ SOURCE TERM


Lambert, G., Pollan, G., Ardoin, B., Rosnet, J. and Balkanski, Y. 1995. CTR database of $^{222}\text{Rn}$, $^{220}\text{Rn}$, and $^{218}\text{Po}$ in the sub-Antarctic and Antarctic atmosphere. Centre des Faibles Radioactivites, Gif-sur-Yvette, France.


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Appendix C

Use of a latitudinally-dependent $^{222}$Rn emission distribution for improving atmospheric transport model validations

L.B Robertson, D.S. Stevenson and F. Conen
School of GeoSciences, University of Edinburgh, UK

Introduction
Atmospheric transport models have now reached a stage of development where improved knowledge of the magnitude and distribution of radon-$^{222}$Rn emissions is needed for more accurate validations and parameterisations. Due to the lack of sufficient data, a spatially uniform emission rate of 1 atom cm$^{-2}$ s$^{-1}$ from all ice free land surfaces (land between 60°S and 70°N) is generally assumed. $^{222}$Rn emissions can vary by a factor of up to 3 on the regional scale, however; thus modelled $^{222}$Rn mixing ratios can be in significant error for some locations.

A recent analysis (Conen & Robertson, Tellus, 54B, 127-133) of indirect $^{222}$Rn emission data suggests there is an approximately linear decrease in $^{222}$Rn emissions with increasing latitude in the northern hemisphere, from $\sim$ 30°N. To examine if it might be useful to incorporate this information in future model validations, we have carried out a comparison of observed and modelled long-term mean surface $^{222}$Rn mixing ratios using two different $^{222}$Rn emission distributions: one that is spatially uniform and one that decreases linearly with increasing latitude in the northern hemisphere. The importance of disregarding seasonal variability in $^{222}$Rn emissions in model validations is also investigated.

Results
Fig. 1 shows maps of the differences between simulated $^{222}$Rn mixing ratios. The largest differences occur north of 30°N and over the centre of the continents in particular, as would be expected.

The differences in mixing ratios also extend upward through the atmosphere, with differences between 50-100 x 10$^{-22}$ mol mol$^{-1}$ up to $\sim$ 6 km (Fig. 1c). Observed and modelled mixing ratios are compared for 3 areas of geographic coverage in Table 1.

Table 1: Comparison of model-observation ratio of $^{222}$Rn mixing ratios for uniform and northwards-decaying $^{222}$Rn emission distributions (% of observations).

<table>
<thead>
<tr>
<th>Geographic Coverage</th>
<th>Uniform</th>
<th>Northwards-decaying</th>
</tr>
</thead>
<tbody>
<tr>
<td>North of 30°N</td>
<td>1.32</td>
<td>1.00</td>
</tr>
<tr>
<td>South of 30°N</td>
<td>1.33</td>
<td>1.01</td>
</tr>
<tr>
<td>Global</td>
<td>1.33</td>
<td>1.01</td>
</tr>
</tbody>
</table>

For locations north of 30°N there is a significant improvement in the match between model and observations, with the mean-model observation ratio reduced by $\sim$ 50%, and almost equal to 1. The root-mean-square-error is also reduced by half. This improvement is also significant for global coverage, but there is no difference in model performance for locations south of 30°N, as we would expect.

Fig. 2 shows observed and modelled monthly-mean mixing ratios for four coastal/marine sites. The model reproduces a seasonal cycle at all sites, thus illustrating the dominant influence of meteorology on mixing ratios; however, it does not do this so well for (c) and (d). These discrepancies are probably due to vertical and horizontal model resolution.

Conclusions
- Using the northwards-decaying $^{222}$Rn emission distribution significantly improves the match between model and observations for the surface layer. This also needs to be investigated for vertical profiles, but long-term vertical profile data are sparse.
- Ignoring seasonal variability in $^{222}$Rn emissions in model validations is unlikely to be important for coastal or marine stations; however, it may be important for some continental sites. This also needs further investigation.

Data and Simulations
- Observational data are long-term average $^{222}$Rn concentrations from 17 observatories at different latitudes, ranging from 65°N to 90°S.
- The model used was the UK Met Office global chemistry-transport model (STOCHEM).
- Two model simulations were carried out using:
  1) a 'Uniform' emissions distribution: 1 atom cm$^{-2}$ s$^{-1}$ from 60°S to 70°N
  2) a 'Northwards-declining' emissions distribution: 1 atom cm$^{-2}$ s$^{-1}$ from 60°S to 30°N, decreasing linearly from 30°N to 0.2 atoms cm$^{-2}$ s$^{-1}$ at 70°N.

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