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Atmospheric ^{222}Rn measurements during the 1993 NARE Intensive

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Abstract. In this paper we describe a recently developed technique to collect samples for atmospheric ^{222}Rn measurements suited for deployment on (research) aircraft. Following a technical description of the sampler we present measurements from nine flights during the 1993 North Atlantic Regional Experiment (NARE) intensive over the North Atlantic Ocean and over the continent in the vicinity of Nova Scotia and New Brunswick, Canada. Samples were taken both in the boundary layer and in the free troposphere up to about 5500 m (msl). Concentrations ranged from 0.01 to 1.66 Bq/m^3 in the free troposphere, with means of 1.66 and 0.52 Bq/m^3, respectively. Boundary layer ^{222}Rn concentrations were strongly correlated with back trajectory origins confirming the use of ^{222}Rn as tracer for continental air masses. Samples collected in the marine boundary layer (MBL) were found to be significantly correlated with aerosol particle, NO_y, and O_3 concentrations reaffirming the utility of radon as a tracer of continental boundary layer air. Radon concentrations for the MBL samples were not found to be significantly correlated with transit times from the continent as estimated from back trajectory analysis implying that variations in the radon concentrations are dominated by factors other than radioactive decay. It is suggested that this factor is the height of the continental boundary layer into which the radon is emitted. On the basis of the radioactive decay we estimated apparent ^{222}Rn ages for our samples and discuss the inherent difficulties in reliable age estimates. A comparison with hydrocarbon ratio age estimates for a highly polluted plume of air encountered during the campaign shows a similar age range for these samples and suggests that simultaneous measurements of species with different chemical and physical properties might allow narrowing the uncertainties in such ages estimates.

Introduction

The potential of ^{222}Rn measurements for studying atmospheric processes like turbulent vertical mixing and for characterizing air masses by origin (especially continental versus marine air) has been recognized for many years. The source for atmospheric ^{222}Rn is terrestrial. It is not emitted from the oceans or ice in significant amounts and has no atmospheric source. Radon 222 is a daughter product of the ^{238}U decay series and is produced by α decay of ^{226}Ra ($T_{1/2}$ = 1600 years). Decay products of ^{222}Rn ($T_{1/2}$ = 3.825 days) include several short-lived isotopes, ^{210}Pb ($T_{1/2}$ = 22 years) and finally the stable ^{206}Pb. All of these daughters are chemically reactive charged ions and soon after production irreversibly associate with aerosol particles. Average emission rates of ^{222}Rn over land are estimated to be about 0.7 to 1.3 atoms cm^{-2} s^{-1} [*Wilkening and Clements*, 1975; *Sanak et al.*, 1978; *Liu et al.*, 1984]. Emission from the oceans is 2 to 3 orders of magnitude lower [*Broecker* et al., 1967; *Larson and Bressan*, 1978].

Being, a noble gas, radon is not lost from the atmosphere by deposition, or by chemical reaction; the only atmospheric sink is radioactive decay. Atmospheric ^{222}Rn concentrations are therefore determined by the distribution of radon sources, in relationship to the transport and mixing, processes a given air parcel experiences, and radioactive decay. These characteristics make ^{222}Rn concentration measurements very useful for the study of atmospheric mixing, and transport phenomena. Furthermore, since the half-life of ^{222}Rn is the same order of magnitude as the half-life of atmospheric trace eases such as ozone and NO_x, ^{222}Rn measurements can serve as a valuable tool for interpretation of measurements of the distribution of these species in the atmosphere.

Several authors have used ^{222}Rn and its daughter products to support the interpretation of measurements of other atmospheric species. *Dörr et al.* [1983] used ^{222}Rn measurements for interpretation of CO_2 respiration fluxes from soil to separate the vertical flux from horizontal advection of air. The potential of ^{222}Rn measurements for interpretation of atmospheric monitoring programs for ozone and particles was demonstrated by *Whittlestone* [1985]. *Larson et al.* [1972] and *Wilkniss et al.* [1974] have shown good correlations between atmospheric ^{222}Rn concentrations and air mass trajectories calculated from satellite photographs demonstrating the usefulness of ^{222}Rn measurements for identifying air masses originating from

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continental boundary layers. *Hansen et al.* [1990] state that ^{222}Rn measurements are more sensitive to quick, short-lived changes in flow than are trajectory calculations because most trajectory models are not sensitive to short-duration subsynoptic meteorological events. Several authors investigated the long-range transport of continental air masses across the oceans [e.g., *Prospero and Carlson,* 1970; *Polian et al.*, 1986; *Kritz et al.*, 1990].

Radon 222 simulations are frequently used to evaluate parameterizations of vertical mixing or long range transport in general circulation models [e.g., *Brost and Chatfield,* 1989; *Feichter and Crutzen*, 1990; *Heimann et al*, 1990; *Jacob and Prather*, 1990; *Genthon and Armengaud*, 1995]. Most of these authors state that radon is an excellent tracer for testing transport in these models and that it would be highly desirable to obtain more radon observations in a systematic fashion. Unfortunately, only a very limited number of upper air observations are available to date [*Liu et al.*, 1984].

In this paper we describe a recently developed prototype of an aircraft sampler for atmospheric ^{222}Rn measurements. Following a technical description of the sampler we present and discuss measurements taken during the summer 1993 North Atlantic Reaional Experiment (NARE) intensive. A comparison with simulations using a regional tracer transport model is presented by *Lin et al.* [this issue].

Sampling and Measurement Procedure

For measurement of atmospheric ^{222}Rn concentrations, two approaches are possible. Air samples can be collected and subsequently analyzed in the laboratory through direct measurement of the α decay in scintillation cells, as for example described by *Lucas* [1957], or in ionization chambers [e.g., *Fischer*, 1976; *Roether and Kromer*, 1978]. Another possibility is measurement of the short-lived ^{222}Rn progeny. For this purpose, air is pumped over filters to collect the ^{222}Rn daughters which are attached quantitatively to aerosol particles [e.g., *Busigin et al.*, 1980]. Either the β activities of ^{214}Pb ($T_{1/2}$ = 26.8 min) and ^{214}Bi ($T_{1/2}$ = 19.7 min) or the α activity of ^{218}Po ($T_{1/2}$ = 3.05 min) and ^{214}Po ($T_{1/2}$ = 1.6 x 10^{-4} s) [e.g., *Larson et* al., 1972; *Reineking and Porstendöerfer*, 1990] can be determined from which the original ^{222}Rn concentration can be reconstructed. The latter approach allows for quasi-continuous measurements; however, time resolution is limited by counting statistics and is typically of the order of 15 to 30 min. In addition, one has to assure radioactive equilibrium of radon and its progeny, as well as negligible (or at least constant) loss of aerosol particles in the sample intake system.

Since one of our design goals was a short sampling time (less than 3 min) we chose to collect ^{222}Rn samples and measure their activity later in the laboratory. Because radon ambient ^{222}Rn concentrations at their highest (in the continental boundary layer) are only 5 Bq/m^3 and decrease rapidly with both altitude and distance from the continents, relatively high volumes of air must be sampled to obtain useful measurements (our target was 50 L per sample). As weight and space are often limited on research aircraft, we excluded sampling of air in bags or pressurized tanks and chose to extract ^{222}Rn from the air sample directly on the aircraft by adsorption on activated charcoal [e.g., *Moore et al.*, 1973].

We would like to point out that many of the parameters of the sampling, and extraction system described below apply to the particular approach we chose, and especially to the type of charcoal used. Significant variations in charcoal properties (e.g., ^{226}Ra content and adsorption coefficients) can be found even in different shipments from the same manufacturer, and these variations can have significant influence on the design and operation of a radon extraction system.

Aircraft Sampler

Figure 1 shows a schematic of the sampler. It consists of two 100-w membrane pumps operated in parallel, a bank of 12 stainless steel sampling tubes filled with activated charcoal and an airflow meter (Sierra TopTrack 820 mass flowmeter). A notebook computer controls the pumps and solenoid valves. Upon manual initiation of the sampling cycle, the airflow is integrated by the computer until a preset air-volume has been sampled at which point the computer closes the sampling valves terminating the cycle. At ground level a flow rate of about 35 L/min can be achieved; however, sample flow was found to decrease with altitude. At typical flight altitude, 50-L samples could be collected in 2-3 min. The flow meter was calibrated (in liters per minute at 21°C and 1 atmosphere) by the manufacturer immediately before the 1993 NARE campaign; accuracy of the flow measurement is 2-4% for the range of flows encountered during the campaign. The measured sample volume was converted to cubic meters at standard temperature and pressure (0°C and 1 atmosphere) following the ideal gas law. During the NARE campaign the sampler was mounted in a 19-inch rack on the aircraft and was powered from the onboard 28-v power supply.

Radon 222 is adsorbed at ambient temperature on activated charcoal contained in tubes 2.54 cm in diameter and 65 cm in lengtlh. With a column of these dimensions it is estimated that 99.5% of the ^{222}Rn will be collected [*Wetterauer*, 1994]. These estimates were verified by the experiments summarized in

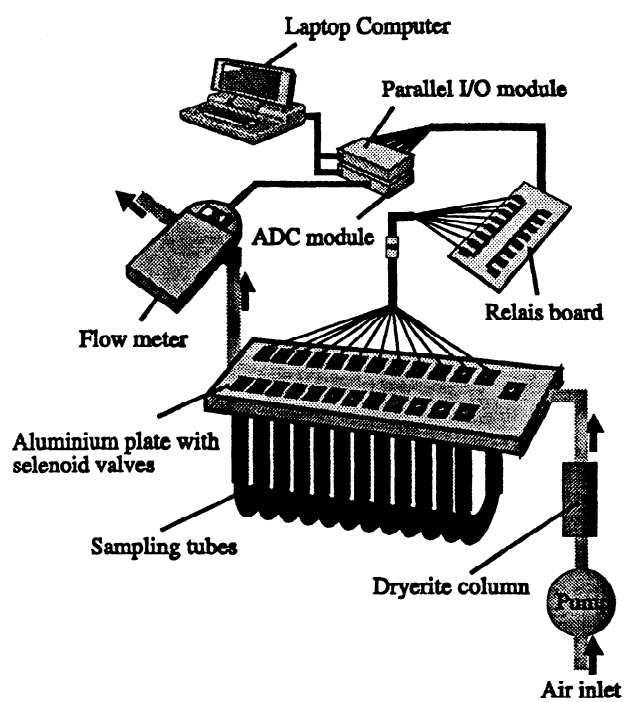

Figure 1. Schematic of the aircraft sampler.

Table 1 in which samples of ambient laboratory air (of unknown radon concentration) were collected over a range of conditions. The radon concentrations in the various samples were identical within 1σ counting statistics except for the 15-cm length column. If it were not, higher concentrations would have been found in the samples taken at low flow rates and low sampling volumes, and different concentrations would have been derived at different flow rates and/or sample volumes. While these experiments did not reproduce ambient conditions, we note that ambient conditions were more favorable for high efficiency for collection of ^{222}Rn than the laboratory experiments because the temperatures, relative humidities, and mass flow rates were all lower.

Initially, water vapor was removed from the airflow with a dryerite column (this approach had been used by *Mathieu et al.* [1988] who verified that dryerite neither emitted nor retained radon). Several laboratory experiments similar to the ones discussed above demonstrated that the ^{222}Rn holding capacity of the charcoal was not significantly reduced by water vapor. In these experiments, samples of laboratory air were collected with the aircraft sampler, with and without the dryerite column. The measured radon concentrations were identical within counting statistics. We thus concluded that removal of water vapor was not necessary and for simplicity, the dryerite column was removed from the system. Although ^{222}Rn extraction from the air sample was still quantitative, the measurement accuracy might have been adversely affected by this modification, as is discussed below.

Extraction System

The sampling tubes were pressurized above surface atmospheric pressure during sampling to prevent contamination with surface air during transfer from the sampler to the extraction system. In addition, diffusive exchange was prevented by two porous metal disks (pore size of 100 μm) at both ends of the columns. Since the volume of the sampling tubes (approximately 150 cm^3 of free air space) was close to the volume of the scintillation cells used for measurement (see below), direct transfer of the collected radon from the sampling tubes into the scintillation cell was not possible, necessitating a second enrichment step.

Table 1. Laboratory Tests to Assure Quantitative Radon Collection and Reproducibility at Different Sample Volumes, Flow Rates, and Charcoal Column Lengths

Column Length cm	Collected Air Volume L	Airflow Rate L/min	^{222}Rn Concentration Bq/m^3 STP
65	50	20.2	2.6 ± 0.3
65	50	19.5	2.3 ± 0.2
65	75	19.8	2.5 ± 0.4
65	100	19.6	2.6 ± 0.3
65	50	26.7	1.2 ± 0.1
65	50	26.8	1.1 ± 0.1
65	50	26.5	1.2 ± 0.4
65	20	9.8	5.8 ± 0.4
65	50	24.1	5.5 ± 0.4
65	50	24.3	5.8 ± 0.4
65	50	24.0	5.9 ± 0.4
65	50	24.2	5.8 ± 0.3
65	50	24.3	5.6 ± 0.3
33	50	24.1	5.8 ± 0.3
15	50	24.0	4.8 ± 0.3

Columns of 65 and 33 cm give equal amounts of adsorbed ^{222}Rn. At 15 cm about 20% ^{222}Rn are lost. Please note that the different radon concentrations during the various measurement series are due to sampling at various locations (e.g., laboratory and outside air).

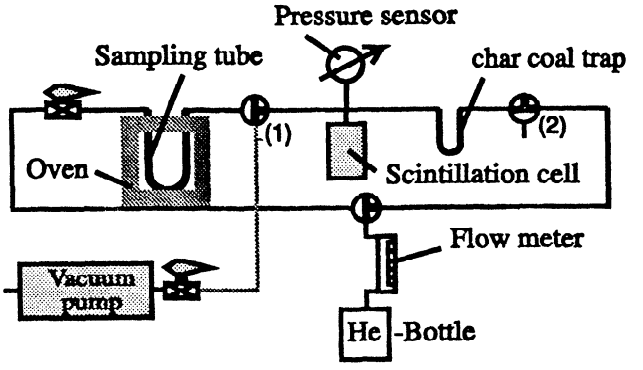

Figure 2. Schematic of the extraction system.

Figure 2 shows a schematic of the extraction system. After insertion of the sampling tubes into the system, they were heated to about 350°C to desorb ^{222}Rn from the charcoal (laboratory experiments showed that even at 250°C, radon release was quantitative). ^{222}Rn was then transfered to a charcoal trap of about 10 cm^3 volume with helium as carrier gas at a flow rate of 0.8 L/min. Transfer time was 5 min and thus a total volume of 41 of helium was used. The charcoal trap was cooled to 0°C during the transfer. The charcoal trap was heated to 350°C and ^{222}Rn transferred into a flushed (with helium) and evacuated scintillation cell with a reversed carrier gas flow. After flushing with helium and evacuation of the scintillation cell, the charcoal trap was heated to 350°C and ^{222}Rn transfered into the cell with a reversed carrier gas flow. After ambient air pressure was reached in the cell, it was closed off and inserted into a scintillation counter.

Theoretical estimates and laboratory experiments as discussed above were performed to verify that extraction and transfer of radon to the counting system was quantitative. In laboratory experiments, either the sampling tube or the charcoal trap were immediately extracted a second time into a separate scintillation cell. Only background concentrations were found in the samples from the second extraction and we conclude that no radon had been left behind in either the sampling, tube or the charcoal trap with our extraction procedure. These and other experiments in which the extraction process was simulated without an actual sample also showed that there was no blank contribution from radon production in the charcoal trap (see discussion below).

In another experiment a known amount of radon (from a gas standard) was injected into a carrier gas flow of helium connected to a sampling tube. This "simulated" sample was then transferred to a scintillation cell using the standard procedure described above. Subsequent measurement yielded the same count rate (within counting, statistics) as when the radon standard was injected directly into the scintillation cells, again confirming quantitative transfer of radon from the sampling to the counting system. These and other experiments are described in more detail by *Wetterauer* [1994].

Counting System

The measurement system consists of a set of scintillation (or Lucas) cells [*Lucas*, 1957] and photomultipliers. For each ^{222}Rn decay, three α particles are registered from the decays of ^{222}Rn itself and its progeny ^{218}Po ($T_{1/2}$ = 3.05 min) and ^{214}Po ($T_{1/2}$ = 1.6 x 10^{-4} s). Since progeny decays are not statistically independent of ^{222}Rn decay, their contribution to the overall counting statistics is minimal [*Sarmiento et al.*, 1996]. Typically, samples were counted for to 19 hours. Total counts were recorded every 30 min with a microcomputer to allow detection of irregularities (e.g., because of power interruptions).

Background count rates were determined for each cell/counter combination to be between 2.30 ± 0.7 and 5 ± 1.0 mBq. Efficiencies of the counter and cell combinations were determined using a gaseous radon standard and were typically greater than 90%. The radon standard consisted of a glass container with a volume ^{226}Ra of about 20 L filled with helium in secular equilibrium with a NBS ^{226}Ra solution. The ^{222}Rn activity of the standard was 3 ± 0.06 Bq/L [*Mathieu et al.*, 1980]. Both background and efficiency measurements were interspersed with sample measurements throughout the NARE campaign.

Blanks and Reproducibility

Activated charcoal contains small amounts of ^{226}Ra which decays with a half-life of 1600 years into ^{222}Rn. Before a flight the sampling tubes were heated to 350°C and flushed with helium to remove any ^{222}Rn that had been produced since the last extraction. However, even in the relatively short period of time between sampling and extraction (typically 4 to 8 hours during the NARE campaign) a non negligible amount of ^{222}Rn was produced. To quantify this blank contribution, sampling tubes were cleaned, as described above, and then stored. After various time periods, the sampling tubes were extracted and analyzed; these measurements (a total of 40) are shown in Figure 3. The theoretical ingrowth curve,

$$A_{Rn}(t) = A_{Ra}(t=0)\frac{\lambda_{Rn}}{\lambda_{Rn}-\lambda_{Ra}}(e^{-\lambda_{Ra}t} - e^{-\lambda_{Rn}t}) , \quad (1)$$

where A and λ denote the activities and decay constants of the species and t as time was fitted to the data using a least squares fit. We find a ^{222}Rn equilibrium concentration (for $t \rightarrow \infty$) of

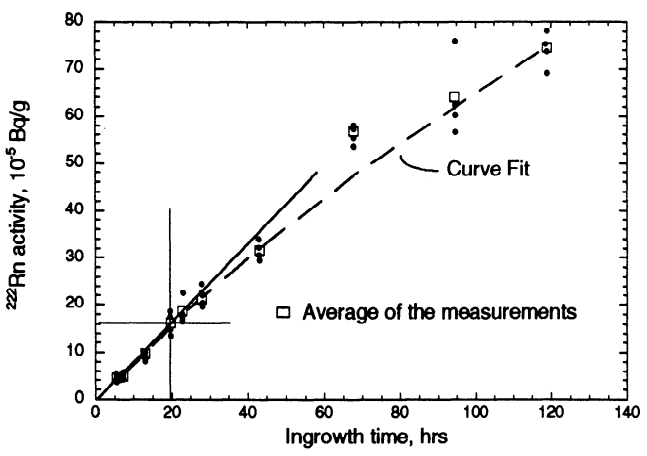

Figure 3. Charcoal blank.

Table 2. Charcoal Blank As Determined With Ionization Chambers and Thus Eliminating a Second Enrichment Step

Ingrowth Time hours	Measured ^{222}Rn Activity mBq	Calculated Equilibrium Activity mBq/g
12.5	14.2 ± 0.6	1.17 ± 0.05
17.5	19.0 ± 1.1	1.15 ± 0.07
28.0	30.9 ± 1.5	1.22 ± 0.06
42.0	43.9 ± 1.8	1.21 ± 0.05

(1.21 ± 0.09) mBq/g of charcoal. A linear approximation of the ingrowth curve for the first 20 hours gives a blank contribution of approximately 0.0085 mBq/g of charcoal per hour. With a 130 g of charcoal and a typical ingrowth of 8 hours this lead to a charcoal blank of about 9 ± 1 mBq. The charcoal blank was also estimated by measuring ^{222}Rn concentrations in collection tubes carried aboard the aircraft and treated identically to the sample tubes, except for exposure to ambient air. Based on 11 such measurements, a charcoal blank of 11.1 ± 3 mBq was determined for the same amount of charcoal and same ingrowth time as above (the larger error is due to the shorter counting times during the campaign measurements and to the smaller number of measurements). These charcoal blank values were more than 10 times as high as measured for previous batches of charcoal from the same manufacturer.

The results of these experiments were used to determine a blank correction for calculation of ambient ^{222}Rn activity. It was assumed that the blank ^{222}Rn activity was proportional to the mass of the charcoal in each of the tubes and to the time since the tube had last been heated and purged with helium (i.e., to the elapsed time since the previous sample had been transferred to the scintillation cell). Because of the unexpectedly high radon production in the charcoal employed in these measurements, this blank contributed significantly to the uncertainty in determination of the ambient radon concentrations, especially the low-level concentrations encountered in the free troposphere.

A further note regarding the uncertainty of our measurements is also in order. In Figure 3 it is apparent that the individual measurements scatter about the ingrowth curve by about 10%, whereas counting statistics predict an uncertainty of 2 to 3%. To identify the source of this additional uncertainty, we repeated the ingrowth experiment in the laboratory using a single extraction tube and ionization chambers instead of scintillation counters. Because of the larger volume of the ionization chambers (1.5 L), radon could be transferred directly from the sampling tube to the counter, eliminating the second enrichment step used to measure the radon activity in the field samples. As may be seen from Table 2, the ^{222}Rn activities measured for a given ingrowth time by this procedure agreed to within counting statistics.

The results of this experiment suggest an additional source of uncertainty (beyond counting statistics) in the procedure that was used to determine the ambient radon concentrations. First it is possible that water vapor transferred from the sampling tubes to the small charcoal trap during the extraction procedure used to analyze the ambient samples might have partially blocked the pore space of the charcoal and prevented quantitative transfer of ^{222}Rn to the scintillation cells. Such an explanation would be consistent with the lower scatter in the second experiment since it did not employ an intermediate trap. The second explanation is that the scatter was due to a difference in the radon production

rate of the various sampling tubes that were used in the ambient sampling system. In the first series of experiments, all 12 sampling tubes were used to determine the radon ingrowth curve, whereas in the second experiment the same sampling tube was used for all of the measurements. Unfortunately, we have replaced the charcoal used for sampling in NARE 1993 and cannot distinguish between these two possibilities.

Since we cannot identify the source of this error, and correct for it, we have adopted a conservative approach for estimating the error in the NARE measurements and have added a systematic error component of ±10% (based on scatter about the ingrowth curve) to the statistical counting uncertainty given below. In the Appendix we summarize the various factors contributing to the measurement uncertainties.

We further examined the uncertainty of our measurement system by comparing the radon activities of 16 sample pairs that had been collected within several minutes of each other (as marked in Table 3) during the NARE campaign. The measured radon concentrations of 8 pairs of these samples was identical to within the statistical counting error (1σ), three within 1.25σ, and one within 1.5σ. The remaining four pairs disagreed by 2, 2.5, 3.5, and 5σ. However, the potential temperature, dew point, aerosol, ozone and CO concentrations measured during collection of the samples constituting the last three sample pairs also disagreed significantly, suggesting that the samples had been collected in air masses with different characteristics. We conclude that our estimates of the overall uncertainty of our measurements are reasonable, although it is clear that data quality could be enhanced in future experiments by collection of duplicate samples.

Results

During the NARE summer intensive in August 1993 ^{222}Rn sampling was conducted with the U.S. Department of Energy (DOE) Gulfstream G-1 aircraft, an intermediate size, twin-turboprop aircraft equipped with an array of scientific instrumentation for measurement of trace gas and aerosol concentrations. The capabilities of this aircraft have recently been described [*Spicer et al.*, 1994]. A detailed description of the configuration and instrumentation of the aircraft as deployed during the summer 1993 NARE program are given by *Daum et al.* [this issue].

The G-1 was stationed at Halifax Nova Scotia, during the NARE campaign. ^{222}Rn samples were collected on nine flights between August 16 and 31, 1993. Altitudes ranged from ≈100 m to ≈5 km (msl); a total of 68 air samples were collected. Although measurements over the North Atlantic Ocean are emphasized, they were also made over Nova Scotia and New Brunswick, Canada. Approximately 25% of the measurements were made under conditions where the synoptic flow was from the marine environment. The remainder of the measurements were made under conditions where the flow was from continental North America. Measurements were relatively evenly split between the boundary layer and the free troposphere. The geographic distribution of the measurements is shown in Figure 4.

Because of the small sampling capacity with our prototype instrument no systematic sampling strategy could be implemented. Instead, we tried to sample air masses which, based on real-time measurements such as aerosol and ozone, seemed of special interest. The sampling locations and measured ^{222}Rn concentrations are given in Table 3 together with a variety of simultaneous meteorological and trace gas measurements. Below we describe some of the features found in the ^{222}Rn data. Thereafter, the results from two selected flights are discussed in detail. All radon concentrations are given in units of Bequerel per cubic meter at standard temperature and pressure (Bq/m^3 STP).

Radon Concentrations and Their Variation With Altitude

A composite vertical profile of the ^{222}Rn activity for all radon samples collected during the program is given in Figure 5. Overall, the vertical profile exhibits a general decrease in ^{222}Rn activity with altitude, although very low concentrations were observed at low as well as high altitudes. Frequency distributions of the radon activities divided into groups designated as having been collected in the boundary layer and in the free troposphere are shown in Figure 6. For purposes of these plots, boundary layer samples were defined as those collected below 2 km with dew points 0°C; free troposphere samples were identified as those collected above 2 km or with dew points 0°C. Mean concentrations of samples identified as boundary layer were 1.66 Bq/m^3 and ranged between 0.17 and 4.77 Bq/m^3 whereas the mean concentration for free tropospheric samples was 0.52 Bq/m^3 and ranged between 0.01 and 1.66 Bq/m^3. The difference between the mean boundary layer and the free troposphere radon activities is consistent with a boundary layer source for ^{222}Rn. The occasional high values of ^{222}Rn in the free troposphere indicate the occurrence of sporadic transport from the boundary layer to the free troposphere.

The vertical profile of ^{222}Rn constructed by considering only the highest activities in a given altitude range (as indicated by the dashed line on the right-hand side of the envelope of circles in Figure 5) is very similar, both in terms of the magnitudes of the radon activities and with respect to their variation with altitude, to the summertime mid continent profile shown by *Liu et al.* [1984]. The vertical profile constructed by considering only the lowest concentrations measured within a given altitude range (as indicated by the dashed line on the left-hand side of Figure 5) is very similar to the vertical profiles shown by *Andreae et al.* [1988] for measurements made in the late spring over the Northeast Pacific Ocean. It is shown below that boundary layer samples corresponding to the "continental" vertical profile are associated with relatively rapid transport of air from the continent to the North Atlantic, whereas boundary layer samples corresponding to the "marine" vertical profile had not been in contact with land for extended periods of time.

Relationship of ^{222}Rn Concentrations To Back Trajectories

Hybrid single-particle lagrangian integrated trajectories [*Draxler*, 1992] were used in this analysis and were calculated remotely on the NOAA computer system using an automated procedure [*R.R. Draxler*, private communication, 1994]. These calculations are based on an archive of forecasts from the National Meteorological Center nested grid model comprised of a time series of +2- to +19-hour forecasts at two-hour intervals generated every 12 hours [*Draxler*, this issue].

Free troposphere samples. With the exception of two samples, 36-hour back trajectories for samples collected in the free troposphere were all from the quadrant between due west and due north of the locations where the samples were collected. Although significant variability is exhibited in the free

Table 3. Radon 222 Trace Gas, Accumulation Mode Aerosol Concentrations, and Sampling and Meteorological Parameters From Nine NARE Flights

1993	Start[a] hours	End[a] hours	Lat °N	Long °W	Alt msl	^{222}Rn Bq/m^3 STP	Age days	O_3 ppbv	CO ppbv	NO_y ppbv	Aerosol[b] cts/cm^3	Temp °C	Dew Point °C	θ °C	Class[c]	Back Trajectory Origin
Aug. 16[c]	16.567	16.602	45.35	67.20	1686	1.42 ± 0.16	6.7	31.7	177	0.58	372.0	16.70	8.32	34.00	BL	NW
Aug. 16[c]	16.611	16.645	45.37	67.39	1686	1.36 ± 0.15	7.0	34.2	179	---	376.0	16.05	8.12	33.36	BL	NW
Aug. 16[c]	16.795	16.836	45.33	67.39	3242	0.58 ± 0.08	11.7	40.9	---	0.59	175.0	4.10	-3.00	37.59	FT	NW
Aug. 16[c]	16.843	16.883	45.25	67.35	3235	0.78 ± 0.10	10.1	39.5	---	---	188.0	4.77	-1.80	38.22	FT	W
Aug. 16[c]	17.115	17.145	45.27	67.68	316	1.55 ± 0.18	6.2	25.0	216	0.78	545.0	26.80	14.90	30.00	BL	W
Aug. 16[c]	17.168	17.199	45.33	67.69	327	2.37 ± 0.27	3.9	24.7	---	---	559.0	25.73	15.25	29.00	BL	W
Aug. 16[c]	18.091	18.131	43.74	66.22	3220	0.76 ± 0.09	10.1	36.1	---	---	105.0	6.44	-4.23	39.90	FT	NW
Aug. 16[c]	18.459	18.489	43.77	66.26	160	1.34 ± 0.16	7.0	29.2	191	0.62	534.0	26.40	14.70	28.00	MBL	N
Aug. 16[c]	18.503	18.533	43.71	66.13	95	1.15 ± 0.13	7.9	28.7	---	---	524.0	25.20	15.10	26.10	MBL	N
Aug. 17	16.810	16.869	44.36	61.23	469	0.25 ± 0.03	16.4	31.8	156	0.33	200.0	17.00	7.30	21.70	MBL	E
Aug. 17[d]	16.971	17.036	44.13	60.60	1550	0.04 ± 0.01	26.4	47.0	199	0.38	114.0	13.10	-17.70	28.80	FT	N
Aug. 17[d]	17.048	17.114	44.01	60.27	1546	0.15 ± 0.02	19.4	31.7	177	0.28	139.0	11.90	-2.40	27.40	FT	NE
Aug. 17	17.306	17.382	43.99	60.01	3088	0.01 ± 0.01	34.1	49.8	---	---	33.0	8.90	-32.00	41.20	FT	NW
Aug. 17[d]	17.751	17.810	44.02	60.08	112	0.19 ± 0.02	17.7	32.4	129	---	185.0	18.00	12.00	19.00	MBL	E
Aug. 17[d]	17.815	17.873	43.94	60.01	116	0.25 ±0.03	16.4	32.6	---	0.42	176.0	18.10	11.80	19.20	MBL	E
Aug. 17[d]	18.174	18.252	44.20	60.80	3067	0.02 ± 0.01	30.2	54.4	213	0.34	59.0	9.60	-30.30	41.70	FT	NW
Aug. 17[d]	18.271	18.348	44.30	61.25	3067	0.17 ± 0.02	18.3	53.7	140	0.29	67.0	8.90	-33.20	40.90	FT	NW
Aug. 18[d]	15.959	16.019	44.51	61.80	39	0.25 ± 0.03	16.4	26.5	---	0.47	122.0	20.60	13.30	26.50	MBL	E/N
Aug. 18[d]	16.025	16.084	44.43	61.50	48	0.36 ± 0.05	14.5	27.0	94	0.44	116.0	20.50	13.40	20.90	MBL	E/N
Aug. 18[d]	16.387	16.455	44.03	60.04	1467	0.11 ± 0.03	21.3	51.0	118	0.53	93.0	16.00	-21.10	30.90	FT	NE/NW
Aug. 18[d]	16.460	16.528	44.04	60.04	1470	0.08 ± 0.02	23.3	51.4	122	0.56	92.0	16.20	-21.60	31.10	FT	NE/NW
Aug. 18[d]	16.691	16.750	43.94	59.95	27	0.17 ± 0.02	18.3	30.7	105	0.40	51.0	20.10	10.20	20.30	MBL	E/N
Aug. 18[d]	16.754	16.814	44.02	59.70	32	0.16 ± 0.02	18.7	30.9	112	0.39	54.0	19.20	10.20	19.50	MBL	E/N
Aug. 22[d]	15.551	15.603	44.21	60.84	5543	0.55 ± 0.06	12.0	41.8	186	---	28.4	-12.20	-30.50	46.00	FT	NW
Aug. 22[d]	15.636	15.686	44.19	60.76	5461	0.67 ± 0.08	10.9	41.0	---	---	36.3	-11.50	-29.90	45.80	FT	NW
Aug. 22[d]	16.607	16.639	44.08	60.54	1567	0.40 ± 0.05	13.8	40.6	162	0.36	35.9	8.90	-17.60	40.64	FT	NW
Aug. 22[d]	16.643	16.677	44.12	60.68	1564	0.18 ± 0.03	18.0	39.3	132	---	43.2	8.50	-17.00	24.10	FT	NW
Aug. 22	16.926	16.958	44.49	61.82	1562	0.20 ± 0.03	17.4	35.6	122	0.37	125.0	8.70	-16.60	24.30	FT	NW
Aug. 22	17.220	17.250	44.79	63.13	705	0.82 ± 0.09	9.8	27.0	97	---	185.0	13.10	5.70	20.00	BL	NW

Table 3. (continued)

1993	Start[a] hours	End[a] hours	Lat °N	Long °W	Alt msl	^{222}Rn Bq/m^3 STP	Age days	O_3 ppbv	CO ppbv	NO_y ppbv	Aerosol[b] cts/cm^3	Temp °C	Dew Point °C	θ °C	Class[c]	Back Trajectory Origin
Aug. 24	13.843	13.874	45.02	64.72	780	1.27 ± 0.14	7.4	34.8	95	0.86	315.0	16.30	6.70	38.80	BL	W
Aug. 24	14.994	15.046	45.05	65.36	5130	0.71 ± 0.09	10.6	50.6	---	0.60	26.0	-6.20	-13.70	55.60	FT	NW
Aug. 24	15.618	15.649	44.43	66.33	477	2.35 ± 0.26	3.9	48.6	167	1.65	298.0	18.10	6.60	27.40	MBL	SW
Aug. 24	16.283	16.322	44.11	66.72	2234	0.37 ± 0.04	14.3	45.2	95	0.50	83.0	10.60	-9.60	41.80	FT	NW
Aug. 24	16.505	16.536	44.21	66.37	458	1.58 ± 0.17	6.1	49.5	163	1.60	315.0	17.70	7.20	27.40	MBL	SW
Aug. 27	14.544	14.574	44.36	64.15	173	2.05 ± 0.23	4.7	33.2	---	---	451.0	23.70	14.30	25.00	BL	NW
Aug. 27	14.778	14.809	44.19	64.71	1062	2.11 ± 0.24	4.5	41.9	211	1.48	787.0	24.50	15.20	35.10	BL	NW
Aug. 27	15.386	15.417	43.22	66.95	900	1.23 ± 0.19	7.5	38.4	369	---	405.0	---	---	---	MBL	NW
Aug. 27	15.893	15.934	42.20	68.67	3732	0.45 ± 0.16	13.0	64.5	---	0.56	10.6	12.00	-25.00	51.80	FT	W
Aug. 27[d]	16.346	16.375	42.08	68.80	151	3.79 ± 0.41	1.3	77.2	249	8.20	1285.0	28.40	16.60	29.50	MBL	W
Aug. 27[d]	16.382	16.403	42.07	68.69	146	4.77 ± 0.55	0.0	75.8	235	13.00	1903.0	28.63	17.10	29.70	MBL	W
Aug. 28	14.053	14.083	44.01	61.88	320	2.14 ± 0.24	4.4	81.0	257	2.20	1215.0	21.70	17.60	20.10	MBL	SW
Aug. 28	14.476	14.518	43.95	61.86	3774	0.38 ± 0.06	14.1	55.3	111	---	29.0	9.45	-19.00	44.30	FT	SW
Aug. 28	14.706	14.742	43.89	62.03	2356	0.81 ± 0.10	9.8	55.0	---	---	214.0	17.30	3.30	36.40	FT	W
Aug. 28	14.815	14.847	43.96	62.05	1288	2.72 ± 0.31	3.1	73.2	238	3.70	1096.0	23.60	14.40	31.40	MBL	W
Aug. 28[d]	14.951	14.982	43.97	61.84	683	2.37 ± 0.27	3.9	83.2	---	---	1094.0	28.50	14.10	30.80	MBL	SW
Aug. 28[d]	15.059	15.090	43.90	62.03	627	2.92 ± 0.33	2.7	120.0	369	7.90	1989.0	27.60	15.30	30.10	MBL	SW
Aug. 28	15.456	15.487	42.80	62.02	625	3.02 ± 0.34	2.5	142.0	437	17.00	2341.0	27.00	15.00	29.30	MBL	SW
Aug. 28	16.176	16.218	42.24	61.95	3103	0.68 ± 0.10	10.9	71.6	---	---	10.3	13.20	-25.60	41.90	FT	W
Aug. 29[d]	14.086	14.140	44.00	61.92	201	2.25 ± 0.27	3.9	31.3	---	1.50	601.0	17.40	14.70	19.30	MBL	NW
Aug. 29[d,e]	14.16	14.24	43.96	61.90	202	2.11 ± 0.25	12.0	31.0	---	1.37	585.0	17.30	14.70	19.30	MBL	NW
Aug. 29	14.453	14.486	43.91	61.86	1618	1.46 ± 0.17	6.6	48.0	---	1.38	218.0	14.00	5.30	30.50	MBL	NW
Aug. 29	14.761	14.801	43.98	62.00	3143	0.44 ± 0.06	13.2	56.0	112	---	32.0	8.00	-26.70	40.80	FT	NW
Aug. 29	14.997	15.046	43.99	62.01	4824	0.48 ± 0.08	12.7	65.0	194	0.67	14.3	-2.50	-38.90	48.65	FT	NW
Aug. 29[d]	15.172	15.225	44.08	61.94	5585	0.46 ± 0.06	12.9	62.8	---	---	13.7	-9.70	-42.30	62.80	FT	NW
Aug. 29[d,e]	15.34	15.39	44.62	61.38	5569	0.55 ± 0.09	4.5	75.0	117	---	17.2	-9.20	-42.50	50.00	FT	NW
Aug. 29	15.813	15.870	45.13	60.91	199	1.14 ± 0.14	7.9	29.9	121	---	92.0	17.60	11.00	29.90	MBL	NW
Aug. 29	16.122	16.151	45.01	61.90	265	1.21 ± 0.14	7.6	30.9	---	---	98.9	19.10	9.90	21.70	MBL	NW

Table 3. (continued)

1993	Start[a] hours	End[a] hours	Lat °N	Long °W	Alt msl	^{222}Rn Bq/m^3 STP	Age days	O_3 ppbv	CO ppbv	NO_y ppbv	Aerosol[b] cts/cm^3	Temp °C	Dew Point °C	θ °C	Class[c]	Back Trajectory Origin
Aug. 31[d]	16.427	16.458	45.30	67.74	1022	1.04 ± 0.14	8.4	59.4	215	1.62	523.0	13.80	11.00	24.00	BL	SW
Aug. 31[d]	16.496	16.528	45.36	67.68	1019	1.26 ± 0.14	7.4	56.5	184	---	517.0	13.80	10.00	24.00	BL	SW
Aug. 31	16.633	16.663	45.32	67.75	345	1.18 ± 0.13	7.7	43.8	131	1.80	304.0	19.50	12.00	22.90	BL	SW
Aug. 31	17.093	17.124	43.99	67.79	1028	1.52 ± 0.16	6.4	58.9	219	---	499.0	15.90	10.70	26.20	MBL	SW
Aug. 31	17.821	17.853	42.48	68.05	930	1.68 ± 0.18	5.8	79.5	259	3.70	990.0	16.50	13.00	25.80	MBL	W
Aug. 31	17.954	17.987	42.48	68.02	1695	1.67 ± 0.20	5.8	---	218	3.50	807.0	14.30	10.80	31.60	MBL	W
Aug. 31	18.100	18.137	42.51	67.98	2620	0.99 ± 0.13	8.7	---	---	2.20	294.0	10.30	2.90	37.40	FT	W
Aug. 31	18.260	18.303	42.48	68.01	3706	0.75 0.09	10.2	---	158	---	87.6	3.93	-7.03	42.70	FT	W
Aug. 31	18.501	18.533	42.39	67.97	1364	2.89 ± 0.32	2.8	87.0	---	6.65	1772.0	15.54	13.23	29.37	MBL	NW

[a]Start and end of sampling interval; local time (GMT+5).
[b]Accumulation mode aerosol concentration measured by active scattering aerosol spectrometer (ASASP).
[c]Classification: BL, boundary layer; MBL, marine boundary layer; FT, free troposphere; see text for explanation how this classification was obtained.
[d]These samples were taken in pairs within a few minutes of each other. Note that even within a few minutes, different air masses can be sampled. This is discussed in more detail in section blanks and reproducibility.
[e]These two samples had most likely been swapped during measurement. This is both indicated by the difference in sampling time (dependent on altitude) and the similar ^{222}Rn concentrations of samples collected at the same altitude. They are reported here in the order we believe to be correct. 100 L STP of air were collected on August 17 and 18 and 50 L STP on all other days.

tropospheric radon activities (Figure 5), there was no clear relation between the direction of the back trajectory and the activity, nor was there any significant difference in activities between samples collected over the ocean and samples collected over the continent. This is not surprising since free tropospheric radon activities are controlled by the extent to which continental boundary layer air mixes into the free troposphere and this is not a strong function of the back trajectory.

Boundary layer samples. As noted above, radon samples collected in the boundary layer exhibited a great deal of variability with the range extending from the low concentrations found in the free troposphere to concentrations equivalent to those measured at mid continental locations. Here we examine the variation in ^{222}Rn activity with back trajectory for the subset of boundary layer samples collected at marine locations. Table 3 gives the time, location, activity, and back trajectory direction for these samples. Back trajectory direction is defined as the direction between the location where the sample was collected and where the back trajectory crossed land; transit time is defined as the time required for the sample to travel from the coast to the sampling location and was estimated from the 6-hour back trajectories. Some of the samples designated as having an eastern back trajectory did not extend back far enough in time to reach land.

Figure 7 shows the average ^{222}Rn activity measured for each of the assigned back trajectories. Considering the region (Figure 4) over which the samples were collected, it is easily understood that back trajectories bringing air from continental locations (i.e., locations from the southwest to north of the sampling region) exhibit average ^{222}Rn activities that are a factor of 10 higher than for samples collected when back trajectories were from the east. The general meteorological situation prevailing when the low-concentration samples were collected [*Merrill and Moody*, this issue] suggests that the associated air masses had been in the marine environment for an extended period of time. The difference reaffirms the use of ^{222}Rn as a tracer of boundary layer continental air and that low radon activities are an indicator of air that has been in the marine environment for an extended period of time. Indeed, the concentrations of trace gases and aerosol particles in samples collected when trajectories were from the east were much lower than concentrations of these species when trajectories were from the continent (Table 3).

Figure 7 also exhibits some interesting differences in the average radon activity between trajectory sectors associated with transport from the continent, with the average activity significantly higher in the W and SW groups than in the NW and N groups. This might be due to the prolonged travel of air masses in the latter group over areas with low radon emissions such as Hudson Bay, or ice-covered subarctic regions. Table 3 also shows that radon activity varies significantly within each group. Such variability may be due to a number of factors. The samples under consideration here have been away from the continent for varying periods of time, and the differences may reflect varying amounts of decay of ^{222}Rn To explore this possibility we examined the relationship between radon activity and transit time. No significant correlation was found suggesting either that transit time estimates based on back trajectories are not accurate enough in the boundary layer or that differences in the amount of radioactive decay are not the principal source of the variability in these data. In principle, these differences in radon activity between back trajectories could simply be a reflection of the differences in radon source

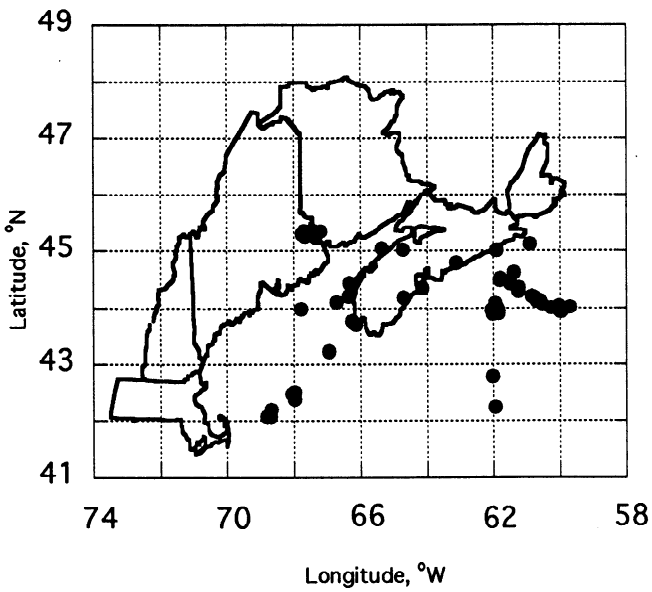

Figure 4. Geographic distribution of the ^{222}Rn sampling sites during the 1993 NARE campaign.

strengths at different locales due to differences in soil type or moisture and similar factors. However, such regional differences should be averaged during the prolonged travel of the air masses towards the sampling site. Unfortunately, insufficient data available to gain any further insight into this issue.

Correlation Between ^{222}Rn and Other Trace Species

Marine boundary layer samples. Marine boundary layer radon activities are related to the concentrations of other trace species that also have a boundary layer source. Figure 8 shows scatter plots of the radon activity as a function of the accumulation mode ($0.15 < d < 3$ μm)) aerosol number density, NO_y, and O_3 concentrations. The species exhibiting the best correlation with the radon activity is the accumulation mode aerosol number density ($r^2 = 0.66$), followed by the correlation

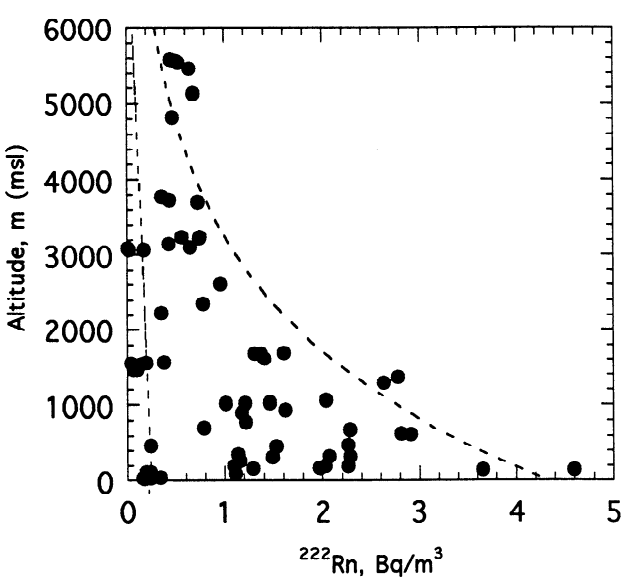

Figure 5. Composite of all ^{222}Rn measurements versus altitude.

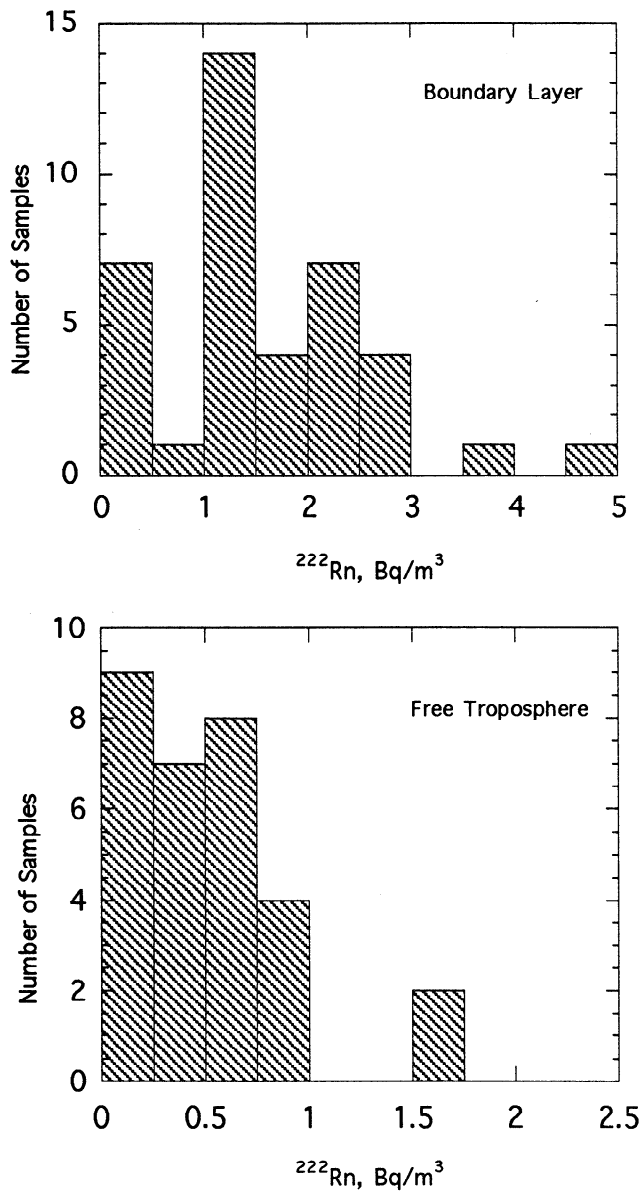

Figure 6. Frequency distribution of ^{222}Rn concentrations found in the boundary layer and free troposphere.

with NO_y ($r^2 = 0.60$) and with O_3 ($r^2 = 0.43$). Although the somewhat lower r^2 for O_3 than for either aerosol particles or NO_y makes some sense because O_3 is not emitted directly into the atmosphere, whereas NO_y, particles, and radon are, the differences in the correlation coefficients are not statistically significant (at the 95% confidence level).

Since measurements were made over a wide range of conditions, and at locations ranging from < 50 to over 800 km downwind of the North American continent, it is interesting to speculate as to why the correlations between radon and these trace species are as good as they are. We recognize, of course, that the primary driver for these correlations is that these species all have continental boundary layer sources and that radon decay is of the same order of magnitude as the removal rate for NO_y and aerosol particles from the atmosphere. Another important driver is that radon as well as the aforementioned trace species are equally subject to the effects of dilution, in particular as determined by the height of the boundary layer into which these

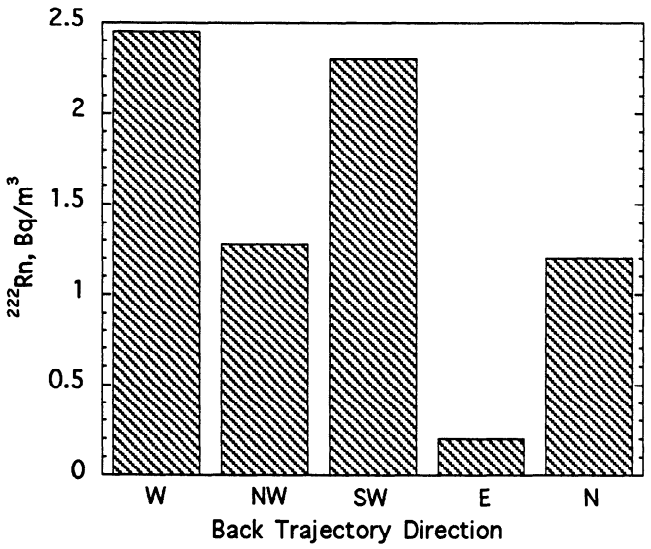

Figure 7. Average boundary layer ^{222}Rn concentrations found for various directions of back trajectory origin.

substances are emitted. It is well known that surface radon concentrations undergo diurnal variation caused by the formation and subsequent breakup of the nighttime inversion which traps radon emissions near the surface, raising the concentrations to several times their mean values [e.g., *Ussler et al.*, 1994]. These same factors influence the concentrations of trace gas and aerosol species emitted at the surface.

We have noted elsewhere [*Daum et al.*, this issue] that continental air transported over the North Atlantic tends to be found in well-defined layers bounded by strong inversions. The presence and persistence of these layers is apparently caused by the temperature differential between the warm continental air and the cold ocean surface which causes the formation of a strong inversion near the ocean surface and stabilizes the atmosphere. The stability of the atmosphere constrains vertical mixing and tends to preserve the structure of the layers as they existed at the land/ocean interface. If for example, transport across the interface occurred early in the day, we would expect that low-altitude layers over the near-coast North Atlantic would exhibit much higher concentrations of radon and associated trace gases than air transported across this boundary late in the afternoon, simply because of differences on the respective boundary layer heights.

To emphasize the importance of this process, we note that the highest radon concentration recorded during the entire program (4.77 Bq/m^3, Table 3) was found on August 27 within the low-level (≈100 m msl) marine inversion about 100 km east of Cape Cod. (For further discussion of this case the reader is referred to *Daum* et al. [this issue]. Considering that the measurement was made in early afternoon and that the back trajectory indicated a transit time of 6 hours from the coast, it may be concluded that this layer was the remnants of a nocturnal boundary layer and that this in part was responsible for the observation of such high concentrations of radon and pollutants. In contrast, ^{222}Rn activity for a sample collected at the same location on August 31 at midday at 930 m msl (Table 3) in a layer trapped between inversions at ≈250m and ≈1500 m msl was 1.68 Bq/m^3. The 1250-m depth of the layer in which this sample was collected, as well as back trajectory analysis indicating that the air was 18 hours from the continent, suggests that this layer was remnant of a fully developed continental boundary layer. O_3 concentrations for these two samples were nearly the same; however, NO_y and particle concentrations for the sample collected on August 31 were a factor of 3.5 and a factor 2 lower, respectively, consistent with the lower radon concentration.

The difference in the radon activities between these two samples cannot be accounted for by the difference in radon decay. The obvious driver, if it is assumed that radon emission rates are reasonably constant is the difference in boundary layer height. That the concentrations of O_3, NO_y, and particles do not change to exactly the same extent as the radon concentrations is not surprising since the sources of these compounds have different geographic distributions and the back trajectories for these samples, while similar, were not identical. It is also reasonable to assume that the chemical processing history of the two air masses was different, leading to, for example, nearly the same O_3 concentrations, for very different NO_y, concentrations.

Differences in the radon activities measured over the North Atlantic due to factors such as the boundary layer depth make difficult, if not impossible, the use of radon activity as a direct estimate of the time elapsed since the air mass crossed the land/ocean interface. For the examples given above, differences in radon activity due only to the difference in transit time as estimated from the back trajectories are of the order of 8%.

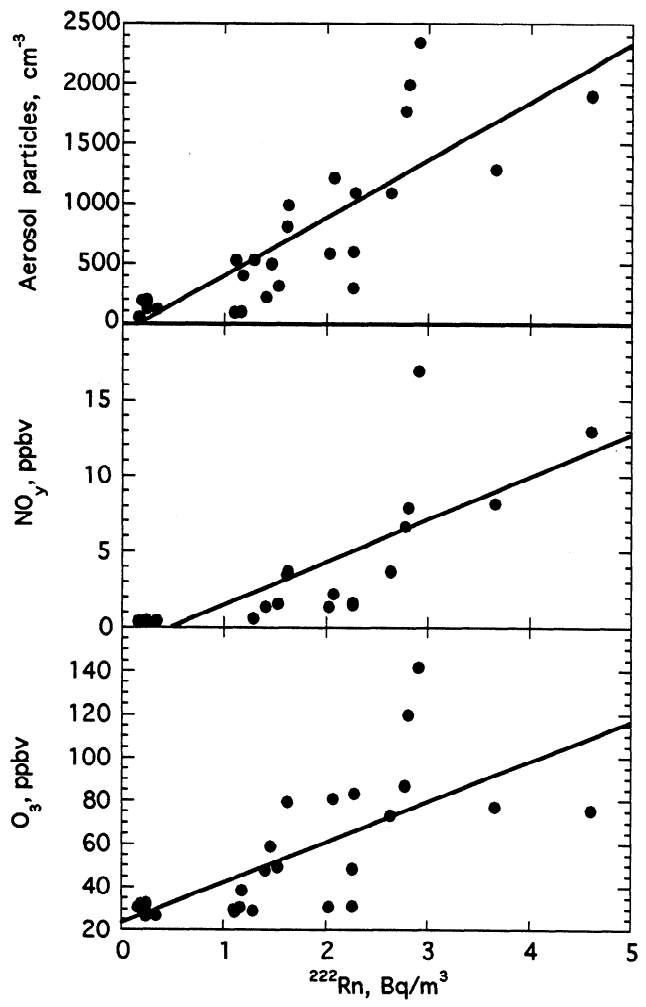

Figure 8. Scatterplots of boundary layer ^{222}Rn concentrations versus accumulation mode aerosol number density, NO_y concentration, and ozone concentration.

Clearly, factors other than radon decay dominate radon activity. Paradoxically, the factors that make radon activities difficult to interpret directly make prediction of radon activities an ideal test for transport models, since to match measured activities the models must correctly predict boundary layer heights, mixing, and transit time.

Free troposphere samples. For samples collected in the free troposphere no significant correlation was observed between the ^{222}Rn activity and the concentration of any other trace species that was measured (aerosol particles, O_3, NO_y, SO_2). This lack of correlation may be for several reasons. First, boundary layer air transported to the free troposphere will be rapidly diluted with air containing varying amounts of O_3, NO_y, and aerosol particles depending on air mass history, and little radon. Depending on the extent to which such dilution occurs, any correlation that existed between radon and other trace species in the boundary layer will be diminished. Second, back trajectories for nearly all of the samples collected in the free troposphere during NARE indicate that the air came to the sampling location from the sparsely populated areas of Canada and the northern United States. These areas are not major sources of pollutants. Under these conditions, good correlation between ^{222}Rn activity and trace species with anthropogenic sources is not expected in the boundary layer, and transporting the boundary layer air to the free troposphere followed by dilution will not improve the correlation.

Apparent ^{222}Rn Age Estimates

Radon 222 is incorporated into an air parcel at ground level. Based on the radioactive decay we can thus calculate an apparent age for a given air mass, estimating the time t since its last exchange with the surface:

$$t = \frac{1}{\lambda} \ln \frac{c_0}{c} \ , \qquad (2)$$

with the radioactive life time $1/\lambda$ = 5.5 days, the radon concentration c at the time of sample collection, and the initial radon concentration c_0. Ideally, these ages should be calculated based on measured initial radon concentrations. Because no such measurements have been done during the 1993 NARE campaign, the ages given in Table 3 were calculated somewhat arbitrarily with the highest ^{222}Rn concentration found during the campaign (4.77 Bq/m^3) as initial surface concentration c_0. This value is somewhat high compared to typical boundary layer concentrations and probably caused by an enrichment of radon in a nocturnal boundary layer (see discussion above). *Liu et al.* [1984], for example, report concentrations of about 3-4.4 Bq/m^3 in the lowest 500 m in a climatological summer profile. If calculated with a mean value of c_0 = 3.7 Bq/m^3, the apparent age estimates would be about 1.4 days lower. It should also be recognized that air mass ages determined in this way tend to be high because any mixing of continental air with the surrounding marine air leads to a reduced ^{222}Rn concentration and thus to an overestimate of the apparent age.

In the given context of measurements in a marine environment these age estimates should not be confused with the transit time from the continent to the sampling site, as "injection" of radon into a given air mass might have occurred at a location along the back trajectory prior to the transition into the marine environment. This is especially true for measurements in the free troposphere. But as pointed out in a previous section, even in the boundary layer we did not find a straightforward relation between transit time and radon concentration. As discussed above, the might reflect that ^{222}Rn concentrations were influenced by the height of the boundary layer into which radon was emitted or by mixing with other air masses, or by inaccuracy of transit time estimates derived from back trajectory analyses.

These problems as well as the strong dependency of the apparent radon age on the initial radon concentration c_0 clearly show that such age estimates cannot be taken literally and can at best give a rough indication of air mass history. It would be interesting, however, to compare these estimates with the "chemical ages" derived from hydrocarbon ratios [*Parrish et al.*, 1992]. This technique has also been applied to the NARE data [*Kleinman et al.*, this issue], but unfortunately, radon and hydrocarbon samples were not collected simultaneously and a direct comparison is impossible.

In Figure 9 we present a plot of ozone concentration versus altitude for all the data points from our flights with simultaneous ^{222}Rn measurements, indicating their ^{222}Rn age by different symbols. It can be seen from the figure that for the flights on which radon samples were collected, a layer of relatively high ozone concentrations existed between about 200 and 1500 m, with highest ozone concentrations found at about 600 to 700 m. The layer appears to be younger than 5 days with most of the age estimates below 3 days (again, these estimates are probably biased toward higher ages because of mixing with maritime air), suggesting a relatively recent boundary layer source for either the O_3 or for the trace species involved in O_3 formation. Most of the age estimates for samples above 1500 m are between 5 and 15 days and suggest relatively little vertical mixing of the air column. A similar low-level layer of high ozone concentrations was found in the data collected on the NCAR Kingair aircraft and hydrocarbon ratios indicate an age range of 0.5 to several

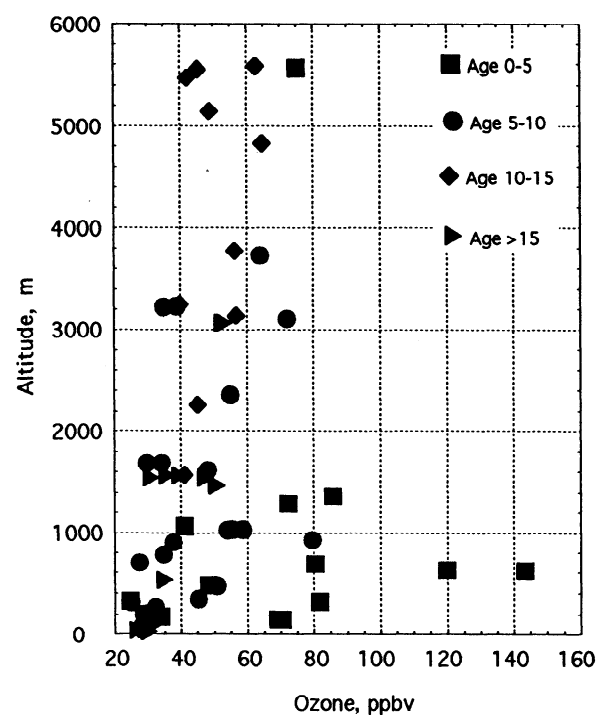

Figure 9. Apparent ^{222}Rn ages for the NARE measurements; exact ages are given for a subset of samples.

days (*P. Goldan*, personal communication, 1995), a somewhat wider range than estimated from the radon measurements.

While viewing the data in the context of hydrocarbon ages gives useful information, hydrocarbon ages are also affected by "contamination" due to mixing, as during a mixing event the concentration of the more reactive of the two gases is relatively more changed that the concentration of the less reactive species (*P. Goldan*, personal communication, 1995). *McKeen and Liu* [1993] have shown that hydrocarbon ratios are affected both by photochemical age and atmospheric transport. Thus combined measurements of various "age-related" parameters of different (chemical and physical) properties will be needed to resolve some of these uncertainties.

Case Studies

On several missions, radon samples were collected for the purpose of obtaining information on the vertical distribution of radon concentrations; on several other flights, interesting features of the ^{222}Rn activity worthy of separate presentation were observed. Two of these case studies are discussed below.

August 28, 1993. On this flight a plume transported from the northeastern United States was sampled at midday. A vertical profile in which several radon samples were collected was made at a 44°N/62°W, and several radon samples were collected during a long transect at an altitude of ≈ 600 m msl between 42° and 44°N latitude along the 62°W longitude line through the transported continental plume. An analysis of this flight is given in more detail elsewhere [*Daum et al.*, this issue]; a description of the synoptic meteorology for this day is given by *Merrill and Moody* [this issue].

Figure 10 shows vertical profiles of ^{222}Rn concentration and corresponding plots of dew point, aerosol number density, and NO_y and O_3 concentrations. These vertical profiles exhibit a fairly polluted layer from the bottom of the profile (≈ 600 m msl) up through about 1800 m msl. Above 1800 m msl the air is much cleaner, as indicated by a significant decrease in concentrations of all of the trace gases as well as the aerosol number density. Dew points are relatively constant up to an altitude of ≈2300 m then decrease; a layer of dry air was observed above about 3400 m msl. Radon activities in the polluted layer between ≈600 and 1500 m msl were quite high, indicating relatively recent transport from the continent. Back trajectories for these samples indicate that the air in which the samples were collected had been over the Connecticut-Long Island-New York area about 48 hours prior to the measurements. This transit time is consistent with the ^{222}Rn activities of these samples (≈2.8 Bq/m^3) leading to an apparent ^{222}Rn age of ≈1.5 ± 0.5 days. Radon concentrations in the free troposphere were much lower than in the polluted (boundary) layer and decreased with altitude. The back trajectories for the samples at 3775 m and 2350 m indicated that the air masses had left the contingent in Maine (12 hours previous) and Connecticut (18 hours previous), respectively, and thus not much prior to the sampling. The nevertheless low radon concentrations point to relatively low vertical exchange along the transport path.

In Figure 11 we show a plot of the ^{222}Rn and O_3 concentrations measured during a constant altitude (625 m msl) flight at a latitude of 62°W between longitudes of 44°N and 42°N. During this flight segment an extensive plume of O_3 and related trace species were encountered (for dtails see *Daum et al.*

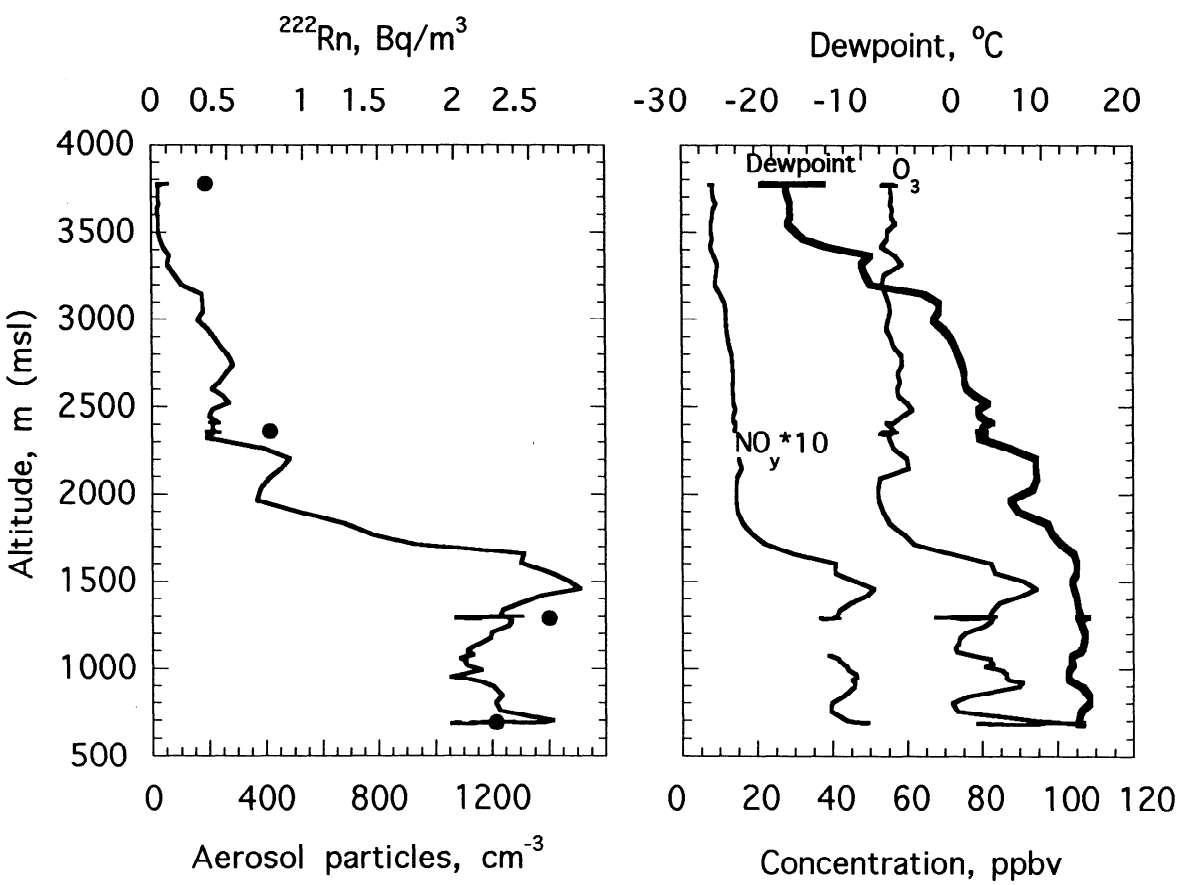

Figure 10. Aerosol particle density, ^{222}Rn (circles) activity, NO_y and O_3 concentrations, and dew point versus altitude for the flight on August 28, 1993.

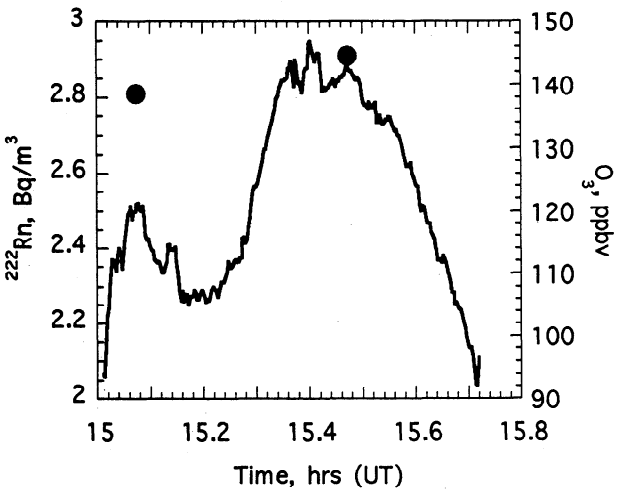

Figure 11. Radon 222 activity (circles) and O_3 concentrations at ≈ 625 m (msl) during a flight segment on August 28, 1993.

[this issue]). Note that ozone concentrations changed significantly between the two samples (both at the same altitude but about 110 km apart). ^{222}Rn activities on the contrary remained constant and thus indicate that the changes in ozone and its precursors could be due to either differences in chemical processing within the same air mass or to spatial variations of the trace species forming O_3.

August 17, 1993. On August 17, 1993, measurements were made in the vicinity of Sable Island, about 250 km south of Halifax, Synoptic conditions for this day are described elsewhere by *Merrill and Moody* [this issue]. Basically, the area was under the influence of a weak high-pressure system over northern Quebec causing low-level winds in the region of the profile to be from the east. Figure 12 shows the radon activities, dew point, O_3, and aerosol number density profiles for a vertical profile near Sable Island. The dew point profile indicates three layers: a moist layer near the surface extending to about 500 m, another moist layer from 500 to 1500 m, and a dry layer aloft. Three distinct layers are also exhibited by the O_3, profile except that the lowest O_3, concentrations are found in the low-altitude layer, and the highest concentrations are found in the highest layer. The aerosol particle profile is very similar to the dew point profile. The high O_3, and low dew point and low particle concentrations observed in the uppermost layer suggest that it may have a stratospheric component.

Radon concentrations measured during this profile are among the lowest measured during the entire program. The shape of the profile suggests that while the air in none of the three layers had been in contact with the continental boundary layer for an extended period of time, the period since such contact was less in the high-altitude sample than for the low-altitude samples. Back trajectories for the low-level samples are from the east although they are truncated because the trajectories run off the National Meteorological Center (NMC) grid required for their calculation. An interesting feature of the profile is the variation in the radon concentration for the middle altitude samples where the radon concentration varied by nearly a factor of 4 at constant altitude. Apparently, these two samples were collected at the interface between the moist low altitude and the dry higher-altitude layers. The low radon concentration sample corresponding to the mixture of dry and moist air with the dry air predominating, and the high radon sample corresponding to a mixture of dry and moist air with the moist air predominating, is indicated by the dew point measurements. The very low ^{222}Rn activity in the highest layer suggests an upper atmospheric

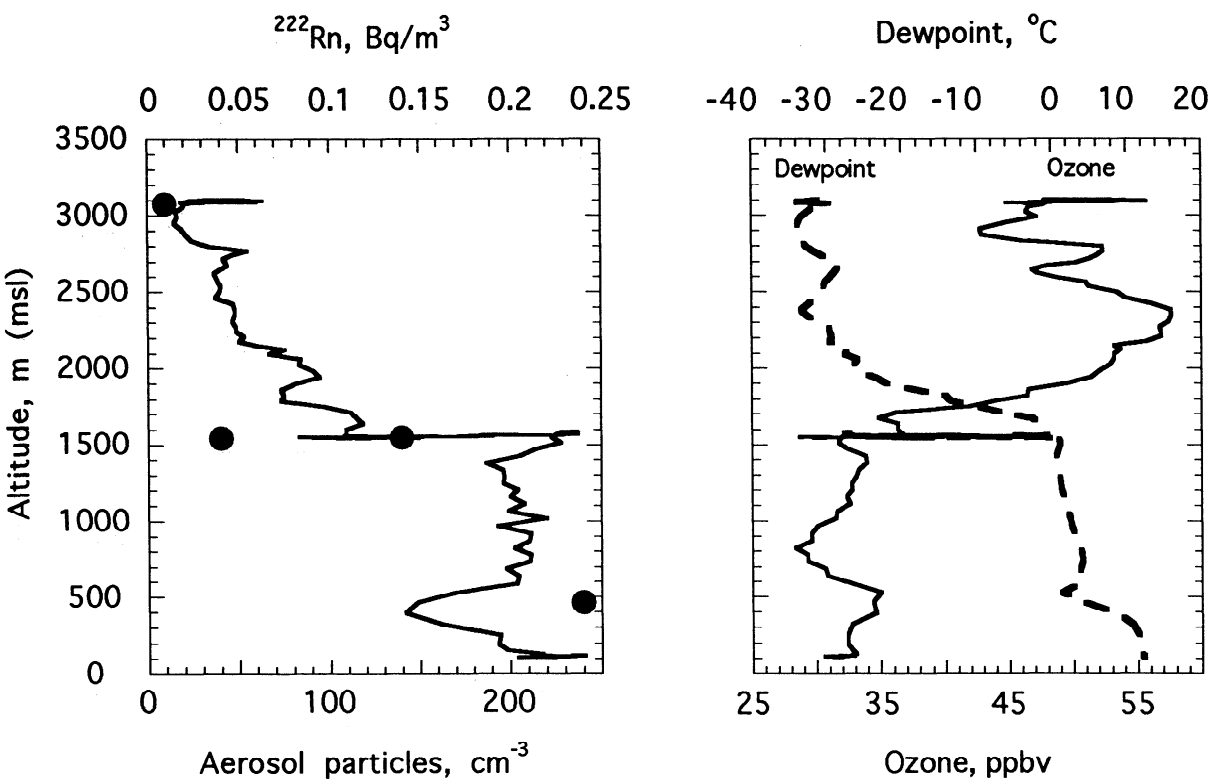

Figure 12. Aerosol particle density, ^{222}Rn activity (circles), dew point, and O_3 concentration versus altitude for the flight on August 17, 1993.

source consistent with the low dew point and elevated O_3, concentration in this layer. The back trajectory for this sample indicates rapid, somewhat descending transport from the NW.

Discussion

In this paper we have presented a series of measurements that once more demonstrate the applicability of ^{222}Rn measurements as an air mass tracer (e.g., as a marker of boundary layer air or of continental versus maritime air). In addition, we discussed how the observed ^{222}Rn activities can be explained by a variety of physical processes in the history of an air mass, such as boundary layer height, dilution, and mixing. This makes radon extremely useful for the evaluation of chemical transport models because these models must accurately describe physical processes that affect both ^{222}Rn concentrations and chemically reactive species to reliably reach conclusions about chemical processing within a given air mass (not affecting ^{222}Rn activities).

Furthermore, we discussed the inherent difficulties encountered in determining the apparent ages (or transit times) of air masses. Simultaneous measurements of age-related tracers such as, for example, radon and hydrocarbons should improve these estimates. We pointed out that these difficulties provide a stringent test for atmospheric models.

Although these benefits have been widely recognized in the past both by experimentalists and by modelers, ^{222}Rn instrumentation has not routinely been included in atmospheric chemistry programs in part because of the unavailability of a simple and efficient technique to collect these samples. In this paper we have described a sampling technique that is both relatively inexpensive and scalable to larger numbers of measurements. In addition, it avoids the uncertainies inherent to indirect radon measurements (based on radon progeny) which are related to potential removal of ^{222}Rn decay products by wet deposition and thus a potential radioactive disequilibrium. Of course, a combination of measurements of ^{222}Rn and its progenies might be most beneficial. It is clear that a larger number of samples must be collected on each flight to give a representative description of the radon distribution in the different air masses encountered.

Subsequent to NARE, we have improved both sampling capacity and measurement accuracy of our radon sampler (this will be described elsewhere). With 24 sampling tubes we can collect one sample every 10 min during a 4-hour flight. We think that a further doubling of this capacity would be desirable and possible in the future. We would also like to refer to the paper by *Lin et al.* [this issue], discussing the comparison of our ^{222}Rn measurements with simulations with a three-dimensional regional transport model.

Appendix: Error Calculation

The radon concentration c (in Bq/m^3) for an air sample is given by

$$c = \frac{1}{3}\left((\frac{N}{T} - A_0)\frac{z(T)}{Ee^{-\lambda t}} - A_E \right)\frac{1}{V} \quad . \tag{3}$$

N is the number of α decays counted during the measurement interval T (in seconds); A_0 is the background count rate (in Bequerels); $z(t)$ is a correction for the decay of radon during the measurement interval and can be approximated by a Taylor series to $z(T) = 1 + \frac{\lambda}{2}T$ (with less than 1% error for measurement intervals less than 13 hours); E is the efficiency of the system; $\lambda = 2.098^{-6}$ s^{-1} is the decay constant for ^{222}Rn; t is the time between sample and start of the measurement; A_E is the radon activity due to radon production in the charcoal (in Bequerels); and V is the sample volume (in cubic meters). Three α decays are counted for each ^{222}Rn decay due to two short-lived radon progenies leading to the factor 1/3.

An error propagation calculation

$$\Delta c_r = \sqrt{\left(\frac{\partial c}{\partial N}\Delta N\right)^2 + \left(\frac{\partial c}{\partial A_0}\Delta A_0\right)^2 + \left(\frac{\partial c}{\partial E}\Delta E\right)^2 + \left(\frac{\partial c}{\partial A_E}\Delta A_E\right)^2 + \left(\frac{\partial c}{\partial V}\Delta V\right)^2} \tag{4}$$

leads to an uncertainty estimate Δc_r due to random errors of

$$\Delta c_r = \frac{1}{3V}\sqrt{\left(x\frac{\sqrt{N}}{T}\right)^2 + \left(x\Delta A_0\right)^2 + \left(ax\frac{\Delta E}{E}\right)^2 + \left(\Delta A_E\right)^2 + \left((ax - A_E)\frac{\Delta V}{V}\right)^2} \tag{5}$$

with

$$x = \frac{z(T)}{Ee^{-\lambda t}} \qquad a = \frac{N}{T} - A_0 .$$

Background count rates were of the order of 4 ± 0.8 mBq. This uncertainty is small compared to typical count rates of >50 mBq. Uncertainty in the sample volumes were of the order of ±2.5% and a similar uncertainty was found for the efficiency of the system. The statistical (counting) uncertainties were typically 2-3%. However, for samples with very low radon content the contribution of the radon blank of the charcoal is dominant and thus leads to a much larger error estimate for the radon concentration of those samples, especially for longer ingrowth times of the charcoal blank. For example, for a sample with a radon activity of 0.4 Bq/m^3, a counting interval of 10 hours, and a charcoal blank of 0.08 Bq (after 23 hours ingrowth), we find a total activity of 0.1 ± 0.003 Bq for a sample volume of 50 L. Even with the assumption of no error due to background and charcoal blank, this would lead to a radon activity of the air sample of 0.02 + -0.003 Bq and thus an uncertainty of 15%. Table 4 shows typical values of error contributions for three samples collected and analyzed during the NARE 1993 campaign.

In addition to the random errors a systematical uncertainty of ±10% (see above) was added, thus leading to a total uncertainty estimate Δc_t of

$$\Delta c_r = \sqrt{\left(\Delta c_r\right)^2 + \left(0.1c\right)^2} \tag{6}$$

for a sample with a radon concentration c and a random error according to equation (5)

Table 4. Contributions of Various Terms in Equation (4) to the Error Estimate of Three Typical Samples

	Rn Conc	Statist Error	$\left(\frac{\partial_c}{\partial_N}\Delta N\right)^2$	$\left(\frac{\partial_c}{\partial_{A_0}}\Delta A_0\right)^2$	$\left(\frac{\partial_c}{\partial_E}\Delta E\right)^2$	$\left(\frac{\partial_c}{\partial_{A_E}}\Delta A_E\right)^2$	$\left(\frac{\partial_c}{\partial_V}\Delta V\right)^2$
Contribution	0.43	0.06	1.6×10^{-4}	0.5×10^{-4}	3.2×10^{-4}	16×10^{-4}	1.6×10^{-4}
		7%	2.5%	15%	73%	2.5%	
Contribution	1.41	0.16	3.7×10^{-4}	0.5×10^{-4}	15×10^{-4}	11×10^{-4}	7.8×10^{-4}
		10%	1.5%	39%	29%	20.5%	
Contribution	2.78	0.30	11×10^{-4}	0.4×10^{-4}	44×10^{-4}	1.8×10^{-4}	28×10^{-4}
		13%	0.5%	51.5%	2%	33%	

Absolute values are in Bq/m^3.

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