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Ion-induced nucleation around radon daughters in remote Arctic maritime air

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ABSTRACT

Measurements made of radon daughters during the International Arctic Ocean Expedition of 1991 did not usually show the expected decrease in apparent concentration due to losses to the surface when aerosol concentrations were very low. The evidence suggests that except on some occasions after the equinox when the air had been near the North Pole for the previous 5 days, sufficient supersaturations of condensible vapours existed to allow nucleation of new particles on radioactively produced ions. This would drastically reduce the mobility of the ions and therefore surface losses. As a result, the measurement usually gave a satisfactory estimate of radon that was very useful in checking on air trajectory predictions and providing more detailed information on contact of the air with land. The exceptions suggest that the measurement might be quite unreliable in conditions where aerosol and oxidizable gas concentrations are very low such as in the Arctic or Antarctic winter.

1. Introduction

Dr. S. Whittlestone of the Australian Nuclear Science and Technology Organization provided equipment for estimation of radon concentrations during the International Arctic Ocean Expedition of 1991 (IAOE-91). This expedition on the Swedish icebreaker *Oden* left Tromsø in Norway on 1 August 1991, passed to the west of Spitsbergen, then remained in port in Spitsbergen from 8–16 August after which it proceeded northeast from Spitsbergen, then north. The Pole was reached on 7 September, the return path lying between Greenland and Spitsbergen. Measurements concluded on 6 October to the west of Spitsbergen.

Whittlestone's standard method of measuring radon, in use at several atmospheric monitoring stations involves the use of a pre-filter to remove all aerosols and attached radon daughters from the air, which then passes into a 1.2 m^3 "delay tank". To this tank a controlled aerosol having a particle concentration of about 25000 cm^{-3} is added. The products of all subsequent radon disintegrations within this volume become attached to the added aerosol, are caught on a filter and the α-emissions counted. The purpose of the primary filtration and the delay tank is to ensure that radon daughters are in equilibrium with the radon. A much simpler alternative is to omit the prefilter, delay tank and added particles, capturing the aerosol and attached radon daughters on a filter in close contact with an appropriate radiation sensor. Such a system was described over 40 years ago by Haxel (1953) and has been widely used ever since. If it is assumed that there are no losses to the surface and no unattached ions, radon can be estimated accurately. However Whittlestone (1990) has found that when particle concentrations were low, the estimate of radon made directly from the ambient aerosol was also low, sometimes by a very large factor. Measurement of the unattached daughters at the sampling point (90 to 165 m above the sea, though the effective height was less) showed that this was not mainly due to unattached daughters at that level but to their depletion near the surface and the upward spread of this depletion layer through mixing.

The choice for IAOE-91 was between using the very large but accurate and direct method or the

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much smaller, simpler method with a considerably faster time response but which might greatly underestimate radon concentrations if particle concentrations were below 300 cm^{-3}. Space considerations and the desirability of a rapid response demanded the latter course. The equipment consisted simply of a filter with support screen through which air was drawn from an inlet in a tube enclosing a photomultiplier. The photomultiplier recorded flashes from a scintillator in close proximity to the filter surface occasioned by incident alpha particles from radioactive substances caught on the filter. An air pump, gas meter, power supply for the photomultiplier and a data logger integrating one minute counts completed the system. If no radon daughters were lost, the sensitivity of the system was such at the flow rate used of 20 litre min^{-1} that 1 count min^{-1} corresponded to 29.3 m Bq m^{-3}.

As it turned out, median particle concentrations (larger than 20 nm diameter) were only of the order of 50 cm^{-3} during IAOE-91 so that a very considerable underestimate of radon was to be expected. Even worse, from the point of view of using the radon results to interpret changes in aerosol or air chemistry, a very high positive correlation between particle concentrations (or, more specifically, cross-sectional areas since ion capture by collision is involved) was to be expected simply because the lower the aerosol concentration, the greater would be the loss of radon daughters.

This paper will discuss the measurements to see whether they failed as the above experiments would suggest. This is important not only for the use of estimated radon in interpreting IAOE-91 measurements but for assessing the validity of past experiments in remote locations that have used the radon daughter method. There have been many such experiments in remote areas where particle concentrations were generally low. Some typical examples are those of Larson et al. (1972), Polian et al. (1986) and O'Dowd et al. (1993).

2. Experimental and theoretical losses of radon daughters

We first have to examine attachment of radioactive ions to aerosols in order to see how Whittlestone's Cape Grim experiences can be translated to other regions having quite different aerosol properties. This is a difficult problem for many reasons, one of which is the rapid acquisition of water and other molecules by the ions to form ion clusters. Cheng et al. (1992) have shown, for example, that the clusters may achieve nanometre sizes in a matter of minutes in clean humid conditions. Nevertheless, by assuming that there is no clustering and only simple interception of aerosol particles we can at least put an upper limit to the rate of attachment and see how it changes with different aerosol size distributions. That part of the radon decay chain relevant to these measurements is:

^{222}Rn: α emission, halflife 3.82 days

^{218}Po: α emission, halflife 3.05 min

^{214}Pb: β emission, halflife 26.8 min

^{214}Bi: β emission, halflife 19.7 min

^{214}Po: α emission, halflife 0.16 ms

Unless the kinetic energy of a daughter ion produced by these processes is reduced quickly to a low value through attachment to an aerosol particle, passage close to the surface as a result of turbulence may cause it to be lost causing a disequilibrium between radon and its daughters. Errors in estimating radon are therefore a function of both probability of capture by aerosol particles within a given time and the vigour of mixing between the surface and the measuring height.

The probability of capture by an aerosol particle will first be considered. Bricard (1977) has given the following formula for the attachment coefficient $B(d_p)$ in terms of the particle diameter d_p, its cross-sectional area a, the velocity of the ion V (about 200 m s^{-1} rms velocity for atomic weight 200), its diffusion coefficient D (about $4 \cdot 10^{-6}$ m^2 s^{-1} for the same ion) and the mean free path of the ion λ (about $5 \cdot 10^{-8}$ m):

$$B(d_p) = aV/\{1 + d_p V/8D(1 + 2\lambda/d_p). \quad (1)$$

The divisor increases from about 1.3 for 0.1 μm particles to 1.5 for 1 μm particles. It is a reasonable approximation for an aerosol where most of the cross-sectional area resides in submicron particles to use instead the simple formula for the frequency of collision f:

$$f = anVC \quad (2)$$

where n is the concentration of daughter ions per unit volume and C the aerosol number concentration.

For the Cape Grim aerosol, using the mean size distributions given by Gras and Ayers (1983) and assuming a concentration of $25 \cdot 10^6\ m^{-3}$, an area of $10^{-10}\ m^2\ m^{-3}$ is found. A radon concentration of 100 m Bq m^{-3} is typical of Cape Grim background conditions and implies the production of 0.1 ^{218}Po atom $m^{-3}\ s^{-1}$ so that we could assume an equilibrium concentration of the order of $20\ m^{-3}$ in view of the 183 sec halflife. Substituting these values in (2) we obtain a collision frequency of about $3 \cdot 10^{-3}\ m^{-3}\ sec^{-1}$, or $1\ m^{-3}$ per 5 min. The probability that one of these ions will become attached to an aerosol particle within its half-life is therefore low. Because of their longer halflives, equilibrium concentrations of ^{214}Pb or ^{214}Po are correspondingly greater but the proportion lost within a lifetime remains the same.

The ion velocity is likely to be substantially reduced by attached molecules causing a still greater reduction in the attachment rate but this will be offset by the decrease in probability of capture by the surface. Thus, as Whittlestone observed, we would expect considerable losses of ions to the surface, disturbing the radon-radon daughter equilibrium in the vicinity. Away from the surface of course, the rapidity of mixing would determine the extent of disequilibrium. Diffusion alone is far too slow a process to cause an appreciable loss to the surface which must be almost totally controlled by the rate of mixing. For the losses to be substantial the mixing time constant of the near-surface layer must be of the order of 100 sec or less.

Whittlestone (1992) used the simultaneous measurements of radon, radon daughters and CN concentrations at Cape Grim to derive an empirical correction to radon estimates R for that site from radon daughter measurements experiments:

$$R = \text{count}/(0.77 \log C - 0.096). \quad (3)$$

The correction applied only for particle concentrations C less than $300\ cm^{-3}$ and assumes that instrumental background count was negligible. When $C = 1.3\ cm^{-3}$, the correction factor becomes infinite and no counts should be recorded. Concentrations lower than this (down to $0.3\ cm^{-3}$) of particles larger than 20 nm diameter were encountered in the Arctic for a total of 14 h, rather more than 1 % of valid observations.

How do the conditions encountered in the Arctic modify the conclusions relevant to Cape Grim?

(a) The height of the air intake was 27 m above the surface, considerably less than the 90 to 165 m used at Cape Grim making the measurement even more vulnerable to surface losses.

(b) For a given particle concentration, cross-sectional area was typically of the order of half and sometimes only one tenth that at Cape Grim because there were usually few large seasalt particles. Eq. (2) therefore predicts an even lower probability of attachment in the Arctic.

(c) Median particle concentrations were considerably lower than at Cape Grim and minimum values less than one-tenth of those at Cape Grim. Eq. (3) predicts that counts should often be zero or require a very large correction because of losses in the sampling line regardless of losses to the surface.

(d) The well-mixed surface layer was usually far more shallow than at Cape Grim, often not exceeding 100 m. (Nilsson, 1996). This means that losses will be a greater proportion of the total for comparable mixing rates.

(e) Surface roughness was much less in the Arctic than at Cape Grim (on the edge of a 90 m cliff) and wind speeds were generally lower. Nevertheless the wind was usually sufficient (averaging 6 m s^{-1}) to promote some turbulence over the small (2 m) pressure ridges and open leads.

On all counts except the last, radon estimates should have been far more in error than at Cape Grim. Unfortunately no measurements are available that would allow the comparison in mixing rates to be made but it seems likely that when all factors are considered losses to the surface should be at least comparable and more probably greater in the Arctic than at Cape Grim.

The actual measurements will now be examined to see if these expectations were fulfilled.

3. Comparison of mean concentrations of estimated radon with previous results

Direct measurements of radon unaffected by such considerations were made by Samuelsson

et al. (1986) during the 1980 cruise of the "Ymer" in the southern part of the area traversed during the 1991 expedition. They obtained arithmetic means of 89 m Bq m^{-3} in August and 105 m Bq m^{-3} in September. While we would expect the 1991 measurements to be lower because they extended right to the North Pole the arithmetic mean concentrations of estimated radon were actually slightly higher, 116 m Bq m^{-3} for August, September and the first 6 days of October. (The period 7–18 August spent in the immediate vicinity of Svalbard has been excluded from the average). The result immediately suggests that in spite of the above predictions radon was not generally underestimated unless the meteorology of 1980 differed greatly from that of 1991.

4. Correlations between particle cross-sectional area and radon

We can next check on correlations between aerosol cross-sectional area and the radon estimate, expecting a strong positive correlation particularly at low cross-sectional areas on the basis of Whittlestone's experiments. The system for measuring aerosol size distributions has been described by Covert et al. (1996) and they have supplied the measurements quoted in this paper.

1188 Arctic 10-min estimates where the aerosol cross-sectional area was less than 10^{-8} cm^2 cm^{-3} were divided into the ranges: (<2, 2–5, 5–20, 20–100) $\times 10^{-10}$ cm^2 cm^{-3}. For comparison, the Cape Grim aerosol cross-sectional area calculated from the mean size distributions given by Gras and Ayers (1983) was found to be approximately $4 \cdot 10^{-10}$ C cm^2 per cm^3, where C is the particle concentration per cm^{-3}. Thus, the largest cross-sectional area in the above ranges equalled that of 25 cm^{-3} Cape Grim particles. Correlation coefficients between area and radon estimate were respectively -0.19, 0.045, 0.14 and -0.04. The fact that these correlations are neither significant nor consistent suggests that aerosol cross-sectional area had little bearing on the radon estimate. There is of course, an overall tendency for radon and aerosol cross-section to increase together, because the more aged aerosols will have lost more particles and more radon. The important point is that within a category of cross-sectional area there

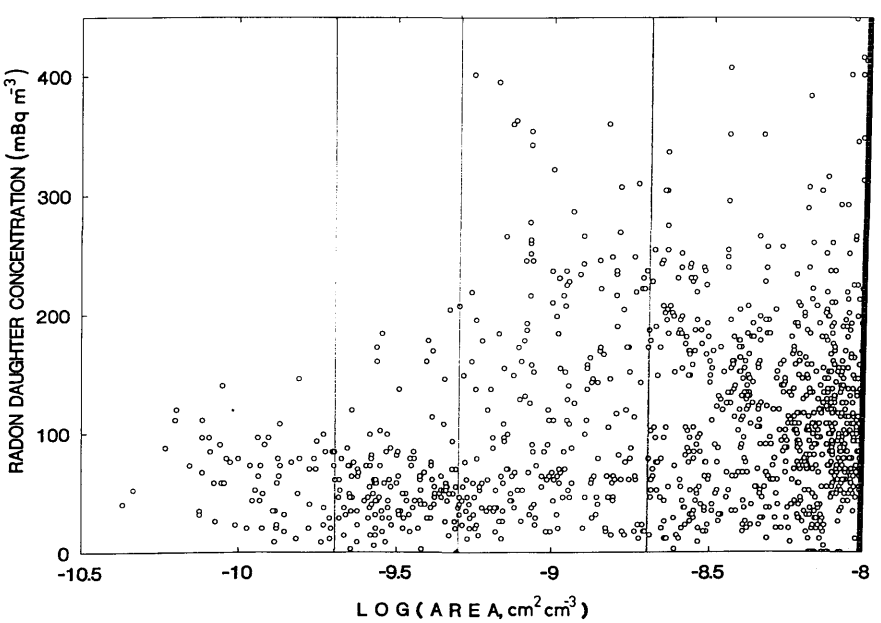

Fig. 1. Estimated radon daughter concentrations corresponding to very low aerosol cross-sectional areas during IAOE 1991.

is no consistent correlation. The scatter diagram of Fig. 1 putting area on a logarithmic scale illustrates these points. On a linear scale, the overall trend would not be obvious.

The conclusion has to be that some factor not included in the above considerations prevented the loss of radon daughter ions to the surface. Alternatively, mixing between measuring height and surface was negligible, which was certainly untrue on all but a few occasions.

5. Cases where no counts were recorded for extended periods

On 26 September, counts from the radon daughter detector quite suddenly tapered off and fell to zero. As this had not happened previously it was at first assumed that the instrument was not functioning but it responded immediately and correctly to an artificial radon source so that after a thorough check operation was resumed and counts then appeared normal. Thereafter counts fell to less than one per hour (corresponding to an estimated radon level of <0.5 m Bq m^{-3}) on 5 separate days for periods ranging up to about 3 h. Such a level seems to be very unlikely as it requires no contact with land for more than a month. This might happen with an intrusion of stratospheric air but ozone measurements and trajectory analysis showed this not to be the explanation. Fig. 2 shows a typical event near midnight on 3 October 1991.

It therefore seems that there were occasions (fortunately few and of short duration) when the predictions of Section 2 were fulfilled.

6. Suggested explanation

Raes et al. (1986) pointed out that the possibility of condensation of sulfuric acid and water on ions in remote atmospheres should not be neglected. They (1992) took these calculations further and showed that ion-induced nucleation rates are about 10^8 times higher than homogeneous nucleation rates, though of course particle formation is limited by the number of available ions. During the IAOE-91 "ultrafine particles" (3–8 nm diameter) were continuously recorded

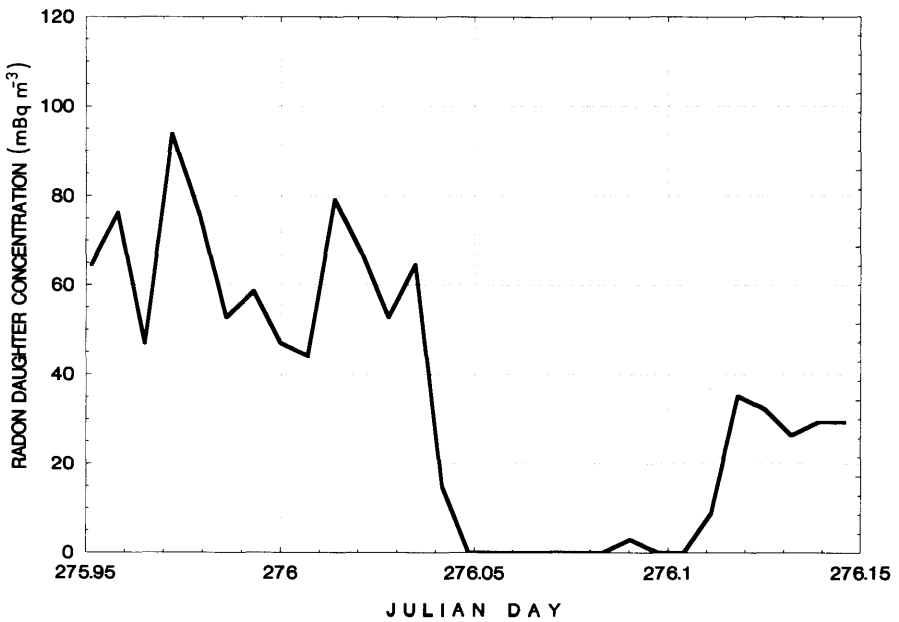

Fig. 2. An example of the sudden decrease in estimated radon that occurred on a number of occasions after 26 September 1991.

and were present in measurable concentrations on 65% of observing time. Their presence indicated new particle generation and a supersaturation of condensible vapours high enough to promote homogeneous nucleation in spite of the reduction of the supersaturation by condensation on existing aerosols. It is therefore reasonable to suppose that lesser supersaturations were frequently present on the remaining occasions and that condensation on ions would result.

This provides an immediate explanation of why radon daughter emissions continue to be measured under conditions in which we would otherwise expect great depletion near the surface, or severe losses in the air inlet system (estimated to be 50% for 3 nm diameter particles). Very low aerosol cross-sectional areas will enhance the probability of supersaturation of condensible vapours such as sulfuric acid and therefore favour particle formation on ions. On this basis the process which prevents loss of ions to the surface or in the air inlet is not attachment but nucleation. (The equilibrium concentration of ions from radon daughters is well below the limit of measurement of ultrafine particle concentrations so that no correlation with radon concentrations would be expected for that reason).

The same considerations provide an explanation of why the counts after the equinox sometimes fell to less than one per hour corresponding to an estimated radon level of <0.5 m Bq m^{-3}. It could simply mean that for a brief period there was insufficient condensible vapour present for nucleation on ions to occur and too low an aerosol cross-sectional area for rapid attachment to take place. The first of these events took place on 26 September when the ship had returned to latitude 83°N. The surface air trajectory lay directly over the North Pole (where the sun had set) and had remained in that vicinity for at least the previous five days. It would not be surprising if there had been a lack of condensible vapours under those conditions for the open leads had refrozen and measurements of dimethylsulfide showed the lowest values of the expedition to that time. In each of the subsequent events also, air trajectory analysis suggested that the air had previously spent a considerable amount of time near the Pole before reaching the ship.

An important test is whether or not ultrafine particles were present during these periods of suspiciously low radon daughter counts. Although present on 65% of all observing time, they were absent during each of the radon episodes referred to.

7. Implications for the radon daughter method of estimating radon in remote areas

Nucleation on the radon daughter ions from a supersaturated sulfuric acid (or other) vapour is likely to be a far more certain way of preventing losses of those ions to the surface than attachment to existing aerosols because it will commence immediately the ion is formed and initial growth will be very rapid. Over the world's oceans we would expect to find sufficient quantities of biogenically produced sulfur gases and OH radical to produce enough sulfuric acid to allow condensation on ions during the summer half of the year. There may, however be a range of aerosol cross-sectional areas for which this is prevented by condensation on pre-existing aerosol but for which capture of the ions by aerosol particles is insufficiently rapid to prevent losses to the surface.

The main difficulty with the nucleation hypothesis is to explain why Whittlestone (1990) found such large losses in a maritime mid-latitude situation. Perhaps extreme mixing rates caused by strong winds impinging on a nearly vertical 90 m cliff only a few tens of metres from the measuring site were responsible. Low particle concentrations at that site are predominantly associated with winter and early spring, the least biologically productive seasons and therefore the ones least likely to have strong supersaturations of sulfuric acid or similar vapours. At that site strong winds (20 m s^{-1} or more) usually accompany the low particle concentrations which occur during surges of Antarctic air.

After the autumn equinox the present results indicate that the method failed at intervals. It seems very likely that failure would be far more frequent through the midwinter period in the absence of direct transport events from lower latitudes carrying aerosol and oxidants. Results obtained under such circumstances clearly have to be viewed with some caution.

The important point for IAOE-91 is that, judging from comparison with the Samuelsson et al. (1986) results, for the greater part of the time,

radon appears to have been estimated with sufficient accuracy to be very useful in detecting such events as brief contacts of the air trajectory with land and mixing between different levels of the atmosphere, in checking the accuracy of air trajectories calculated to pass near radon sources and for providing valid correlations with changes in aerosol concentration.

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