

## CO, CCl<sub>4</sub>, Freon-11, CH<sub>4</sub> and Rn-222 Concentrations at Low Altitude over the Arctic Ocean in January 1974

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### ABSTRACT

Samples of atmospheric Rn, CO, CH<sub>4</sub>, Freon-11 and CCl<sub>4</sub> were taken at various altitudes over the Arctic Ocean north of the Greenland Sea. The concentrations of these components were correlated and interpreted with respect to varying meteorological conditions related to air mass movements. Pronounced concentration gradients were seen in frontal zones, and evidence is found for low-level flow of continental air, both from North America and Europe, into the Arctic region. Comparisons show that Arctic air contains more Rn, CO and CH<sub>4</sub> in winter than in summer. It is suggested that the Arctic Ocean could act as a sink (rather than a source) for atmospheric CO during winter months. The rapid transport of Freon-11 from Europe to the Arctic is also in evidence, while the observed behavior of CCl<sub>4</sub> is difficult to interpret.

### 1. Introduction

The atmospheric trace gases CO, CCl<sub>4</sub>, Freon-11, CH<sub>4</sub> and Rn-222 have been used to study turbulent diffusion, to test atmospheric mixing models, to assess the extent of anthropogenic contributions to the atmosphere, and to investigate atmospheric chemistry. A series of flights of the Naval Research Laboratory's RP-3A aircraft, at an altitude of approximately 300 m between the northern tips of Spitsbergen and Greenland in January 1974, provided a rare opportunity to supplement sparse arctic winter data for these five trace gases.

### 2. Sample parameters

Radon-222 (through its daughter products) was measured aboard the aircraft by a method developed by Larson (1973). The precision of the airborne radon measurements is  $\pm 20\%$  or  $\pm 1$  pCi m<sup>-3</sup>, whichever is greater. In continental air masses, radon concentrations can be as high as 100 pCi m<sup>-3</sup> or more, because radon originates on the continents. The oceanic contribution to atmospheric radon is small; therefore, radon levels in remote oceanic or Arctic areas show background levels  $\lesssim 3$  pCi m<sup>-3</sup>. A doubling of the radon concentration over marine background levels, which indicates the influx of continental air, can easily be detected with our radon method.

Evacuated steel flasks were filled with outside air to a pressure of about 2 atm and returned to NRL to be analyzed for CO, CCl<sub>4</sub>, Freon-11 and CH<sub>4</sub>.

CO and CH<sub>4</sub> were determined by gas chromatography as described by Swinnerton *et al.* (1967, 1968).

Gas chromatography is very precise and accurate for the determination of the two gases in the concentration range encountered during the flights. Precision for CH<sub>4</sub> and CO is  $\pm 0.03$  and  $\pm 0.01$  ppm, respectively. Therefore, the method has been used with great success to detect rather small but very significant differences in the concentration of CO in the marine atmosphere of the Southern and Northern Hemispheres (0.03 and 0.10 ppm, respectively), and can easily measure the much larger differences in CO levels between urban environments (up to several ppm CO) and the true marine environment.

Another gas chromatograph developed by Lovelock (1973) provided the capability to measure Freon-11 and CCl<sub>4</sub> in the samples. The precision of our method for the determination of Freon-11 is about  $\pm 15\%$ . This is sufficient to determine changes in the Freon-11 concentration between true marine air (60–80 parts in 10<sup>12</sup>; abbreviated ppt) and air masses from highly industrialized areas (Europe, North America), in which this exclusively man-made compound occurs sometimes at levels of several hundred ppt. Precision for CCl<sub>4</sub> is the same as for Freon-11, i.e.,  $\pm 15\%$ ; the occurrence of this compound is little understood at this time.

A summary of all precision and accuracy information for the analytical methods used is contained in Table 1 in order to facilitate the interpretation of the significance of the given results.

### 3. Sampling conditions

Meteorological conditions during the three flights and the sampling positions are depicted in Figs. 1–3.

TABLE 1. Carbon monoxide, carbon tetrachloride, Freon-11, methane and radon concentrations over the Greenland Sea and the Arctic Ocean in January 1974.

Sample No.	Date (January)	Time (GMT)	Position	Altitude (m)	CH <sub>4</sub> (ppm*)	CO (ppm)	Freon-11 (ppt**)	CCl <sub>4</sub> (ppt)	Rn (pCi m <sup>-3</sup> )	Temperature (°C)
10	21	1000	71°13'N 15°41'E	5500	—	—	—	—	7.0	-54
11	21	1100	75°20'N 12°59'E	5500	1.63	0.18	97	112	13.9	-50
12	21	1210	80°25'N 11°23'E	305	1.67	0.24	107	153	24.3	-28
13	21	1300	81°28'N 03°21'E	305	1.64	0.24	138	151	74.5	-32
14	21	1354	82°50'N 13°51'W	305	1.68	0.25	118	150	72.4	-32
15	21	1517	78°47'N 09°14'E	7600	—	—	—	—	5.0	-72
16	21	1632	72°23'N 14°47'E	7600	—	—	—	—	2.9	-72
17	24	0826	71°48'N 15°08'E	5500	—	—	—	—	1.7	-50
18	24	0916	76°08'N 01°19'E	5500	1.55	0.12	112	174	2.4	-50
19	24	1040	81°27'N 05°20'E	366	1.60	0.19	107	162	14.9	-35
20	24	1145	83°18'N 20°53'W	366	1.59	0.18	97	142	18.2	-35
21	24	1235	81°56'N 01°20'E	366	1.63	0.20	134	222	14.1	-45
22	24	1412	83°25'N 21°38'W	366	—	—	—	—	10.6	-39
23	24	1625	78°52'N 09°11'E	8200	—	—	—	—	0.3	-71
24	24	1710	75°10'N 12°52'E	8200	—	—	—	—	1.8	-61
25	25	0810	71°08'N 15°27'E	6700	—	—	—	—	5.1	-56
26	25	0900	75°34'N 12°34'E	6700	—	—	—	—	5.9	-56
27	25	1020	81°33'N 07°40'E	366	1.62	0.23	122	153	51.0	-24
28	25	1110	83°24'N 17°31'W	366	1.58	0.20	136	210	26.0	-24
29	25	1217	82°12'N 02°17'E	366	1.61	0.24	82	187	16.0	-21
30	25	1350	83°53'N 25°56'W	366	1.51	0.20	132	170	21.6	-25
30a	25	1415	83°41'N 18°38'W	366	1.61	0.29	148	258	—	—
31	25	1450	82°47'N 01°22'E	366	—	—	—	—	32.0	-21
32	25	1557	79°16'N 09°16'E	8200	—	—	—	—	5.1	-63
33	25	1643	75°33'N 12°36'E	8800	—	—	—	—	2.8	-59
Precision (1σ)					±0.03	±0.01	±15%	±15%	±20%	
Accuracy (1σ)					±0.02	±0.01	±10%	±10%	±30%	

\* ppm=1 part in 10<sup>6</sup>.  
 \*\* ppt=1 part in 10<sup>12</sup>.

The results for the atmospheric trace gas concentrations at the numbered sampling sites of the figures are listed in Table 1.

The meteorological conditions during the three flights were quite different. On 21 January a winter storm was in the area. Thunderstorms with lightning were observed in the morning at an altitude of 5-6 km at about 70N near Norway. In the evening, 78-kt winds were clocked at the airfield at Andenes in northern Norway. On 24 January, another low was situated over the Norwegian Sea and an occluded front was slowly moving northeastward. The sampling area north of 80N was under the influence of a high. The 300-mb charts (~10 km altitude) showed another high over Spitsbergen.

On 25 January, conditions were similar to those of the previous day; however, the front shown over the Norwegian Sea on the 24th had reached the sampling area around noon on the 25th.

4. Results and discussion

The storm on 21 January caused a strong flow of continental air into the sampling area at the 300 m level, most likely from northern Europe and Scandinavia. This is indicated by the very high radon levels, which exceeded 70 pCi m<sup>-3</sup>. The two high radon

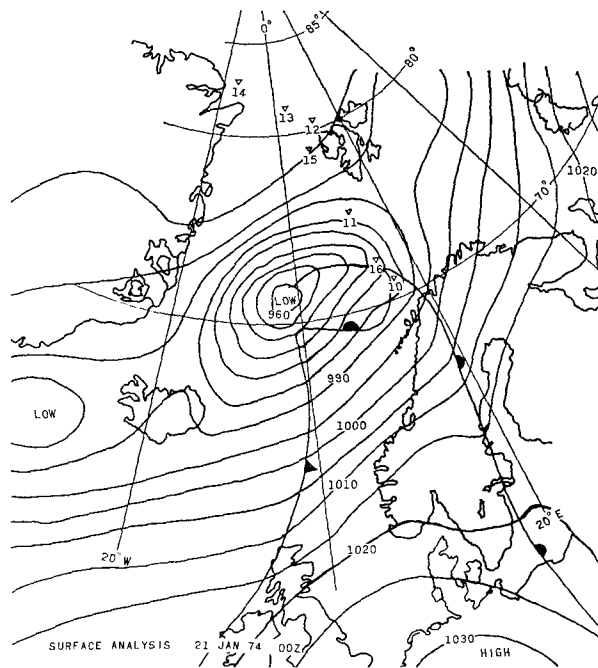


FIG. 1. Meteorological conditions and sampling sites (v) on 21 January 1974.

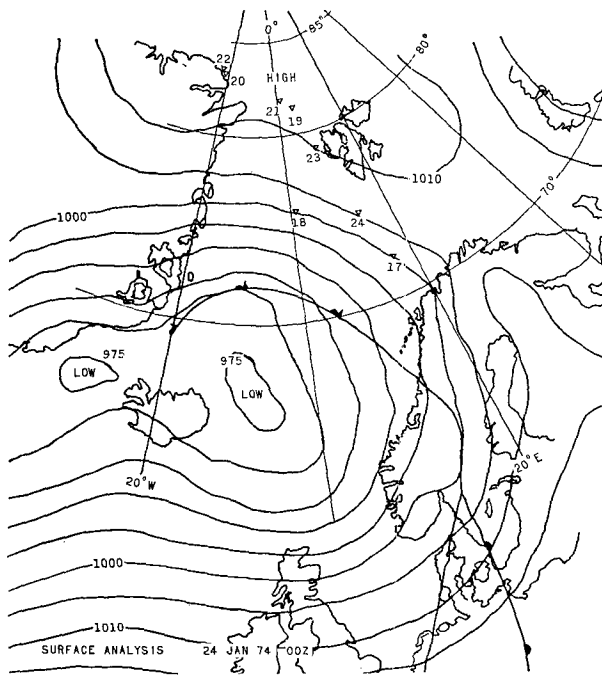


FIG. 2. As in Fig. 1 except for 24 January.

samples (Nos. 13 and 14) showed evidence of very high particulate loadings of the air, which caused dark coloring of the glass fiber filters used for radon sampling. This phenomenon was not observed with any of the other radon filters taken during these flights. On 21 January, CO levels at 300 m averaged 0.24 ppm and the CH<sub>4</sub> averaged 1.66 ppm. These CO and CH<sub>4</sub> levels are measurably higher than the values for the gases on 24 January (CO average 0.19 ppm, CH<sub>4</sub> 1.61 ppm at 366 m). The presence of a different air mass shown by the meteorological charts for 24 January is verified by the much lower radon values (average 14.5 pCi m<sup>-3</sup>), compared to the radon on 21 January (average 57 pCi m<sup>-3</sup>). The arrival of the front on 25 January in the operating area brought a renewed influx of continental air at 300 m (high radon 51 pCi m<sup>-3</sup>, average radon 29 pCi m<sup>-3</sup>), most likely from northern Europe. We observed an increase in CO (average of the 300 m values 0.23 ppm) over the average CO value at the same altitude on 24 January. Methane, however, remained at about the same level (average 1.59 ppm at 300 m) on the 25th as that found on the 24th.

Freon-11 does not show any clear-cut trend; it varies between 82 and 148 ppt (parts in 10<sup>12</sup>). The averages for 21, 24 and 25 January are 121, 112 and 124 ppt, respectively, not significantly different because of the relatively high ( $\pm 15\%$ ) standard deviation. Carbon tetrachloride also exhibits no discernible correlation, the averages at the 300 m level during the three flights being 151, 175 and 196 ppt, respectively, again with a relative standard deviation of  $\pm 15\%$ .

The two samples (Nos. 11 and 18) which were obtained at 5.5 km on 21 and 24 January are best compared to five samples taken between 5.5 and 7.8 km on 19 and 20 January on the flight from Washington, D. C., to Norway via Iceland. These five samples were obtained in a general flow of air from the Pacific area across the United States or Canada into the Iceland area. Sampling was roughly equally spaced between Washington, D. C., and Andoya, Norway, and gave the following average values for the trace gases: CO=0.12 ppm, CH<sub>4</sub>=1.55 ppm, Freon-11 = 128 ppt, CCl<sub>4</sub>=141 ppt and Rn-222=10 pCi m<sup>-3</sup>. Sample 18, taken in relatively clean air (low radon, 2.4 pCi m<sup>-3</sup>), is in excellent agreement with the CO and CH<sub>4</sub> values of those five samples, the Freon-11 may be somewhat lower, and the CCl<sub>4</sub> is higher. Sample No. 11, however, is significantly higher in CO and CH<sub>4</sub> than the five transit flight samples and seems to reflect upward mixing of continental air to the 5.5-km level in the winter storm, as is also indicated by the increased radon level of about 14 pCi m<sup>-3</sup>. Freon and CCl<sub>4</sub> in sample 11 exhibit low values and seem to be consistent with values obtained at 300 m on that day.

The comparison of all the high-altitude samples (5-9 km) with all the low-altitude samples (300 m) confirms that the flow of continental air into the sampling area over the Arctic Ocean occurred at low levels, from a not-too-distant source, most likely Europe and Scandinavia. Correlation coefficients relative to radon were established for all samples taken

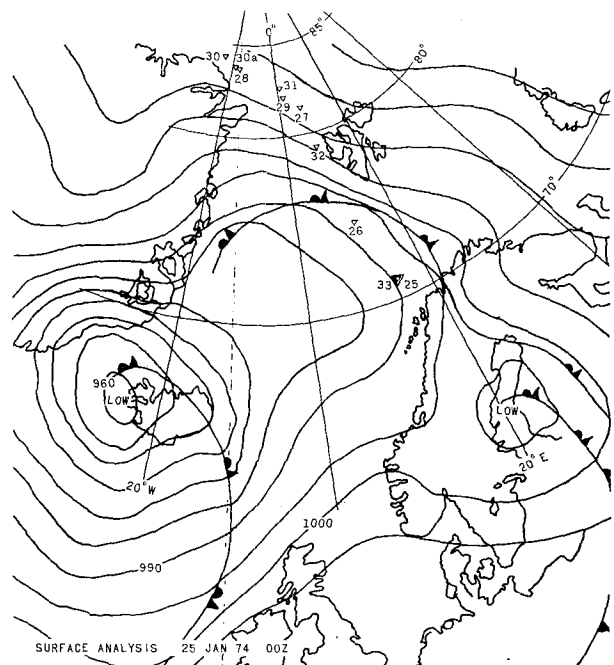


FIG. 3. As in Fig. 1 except for 25 January.

during the flights; the values were 0.70 for CO, 0.52 for CH<sub>4</sub>, 0.46 for Freon-11 and 0.25 for CCl<sub>4</sub>.

If we deem it acceptable to compare atmosphere samples taken aboard ship 7 m above the sea surface with the aircraft samples taken at 300 m above sea level, then we have the opportunity to compare summer and winter data for the Arctic area between Spitsbergen and Greenland. The NRL ship USNS *Mizar* reached 78N at the Greenwich meridian in August of 1971 and our trace gas measurements aboard ship averaged about 3 pCi m<sup>-3</sup> for Rn-222, 1.38 ppm for CH<sub>4</sub>, and 0.09 ppm for CO (Larson *et al.*, 1972). In early September 1972, Rn-222 averaged 6 pCi m<sup>-3</sup> as measured aboard *Mizar* at 81N, 3E (Bressan *et al.*, 1973). The observed seasonal differences in trace gas concentrations seem to be a result of the atmospheric circulation in the Greenland-Spitsbergen area, which is not well defined in the summer, and is dominated in the winter by the Icelandic low with a corresponding southerly flow of continental (European) air. Relatively clean marine or polar air seems to prevail in the summer, while the increase in Rn-222 in the winter, which sometimes exceeds summer values by more than an order of magnitude, documents the pronounced continental influence. A significant increase from summer to winter is also apparent in the CH<sub>4</sub> (from 1.38 to 1.62 ppm) and CO (from 0.09 to 0.22 ppm) data. The summer values for CH<sub>4</sub> and CO can be considered atmospheric baseline values for the Northern Hemisphere. The considerable increase in the Arctic in the winter, especially for CO (a factor of 2.5) has to be attributed to accelerated transport and increased anthropogenic emissions from the densely populated, industrialized areas of the Northern Hemisphere during this cold season.

The different conditions during the arctic winter may also affect the sea-air exchange of CO as the following speculation suggests. CO is produced in the surface waters of the world oceans through biological activity and by photochemical oxidation of organic matter, and in general the ocean surface is a source of atmospheric CO (Linnenbom *et al.*, 1973). During the winter, we can assume a drastic reduction of dissolved CO in Arctic surface waters because of the prolonged absence of sunlight during the polar night and a highly reduced level of biological activity. At the same time, the considerable increase of CO in the atmosphere above ice-free sea water could cause a flux of CO from the atmosphere into the surface water. Thus, during the winter months, the Arctic Ocean could be a sink rather than a source of CO. Finally, a comparison of CO values (0.11 ppm) obtained by Seiler and Junge (1969) during transpolar flights in the winter of 1968 at the 10-km level with our 5–8 km data (CO, 0.12 ppm) implies that the

remote arctic tropospheric CO concentration has remained fairly constant in the past six years.

Freon-11 has no known natural sources; it is exclusively man-made and is released to the atmosphere through its use as an aerosol propellant. It is mainly manufactured in Europe and North America. Based on estimated annual world production rates for Freon-11, calculations by Machta (1973) and measurements by Lovelock *et al.* (1973) in 1971–72 suggest an average Freon-11 concentration of about 100 ppt in the atmosphere of the temperate latitudes of the Northern Hemisphere in 1974. About half of our Freon-11 values (samples 11, 12, 14, 18, 19, 20, 29) agree quite well with this expected value of 100 ppt. The other half is definitely higher, up to 148 ppt (sample No. 30a). This finding seems plausible if we consider that the likely source area for the sampled air was Europe, which accounts for about half of the world's annual Freon-11 output. High values for Freon-11 (160 ppt) in European air masses have also been observed by Lovelock (1973). The findings for Freon-11 suggest rapid atmospheric transport of this compound to Arctic areas in the winter just as for CO. Similar atmospheric transport for Freon-11 at altitude from North America is also implied by the four samples taken in North American air flow between Washington, D. C., and Iceland (19, 20 January 1974). These samples had a Freon-11 average of 136 ppt (individual values were 131, 122, 150 and 141 ppt).

Carbon tetrachloride shows large, uncorrelated variations. The very few measurements of this compound in the environment, and uncertainty about its sources, sinks and atmospheric chemistry, add to the difficulty of understanding its occurrence and behavior.

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