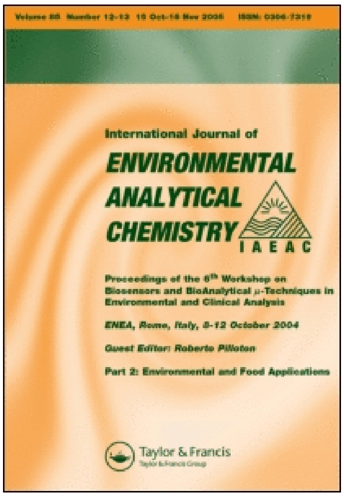


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Hydrogen and Carbon Monoxide at Terra Nova Bay (ANTARCTICA)

E. Corazza[a]; M. Montagnoli[b]; G. Tesi[c]
[a] Istituto Geocronologia e Geochimica Isotopica, CNR, Pisa, Italy [b] Istituto Metodologie Avanzate Inorganiche, CNR, Scalo, Roma, Italy [c] Dipartimento di Statistica, Università di Firenze, Firenze, Italy

To cite this Article Corazza, E. , Montagnoli, M. and Tesi, G.(1994) 'Hydrogen and Carbon Monoxide at Terra Nova Bay (ANTARCTICA)', International Journal of Environmental Analytical Chemistry, 55: 1, 297 — 310

To link to this Article: DOI: 10.1080/03067319408026227

URL: http://dx.doi.org/10.1080/03067319408026227

Intern. J. Environ. Anal. Chem., Vol. 55, pp. 297-310
Reprints available directly from the publisher
Photocopying permitted by license only

HYDROGEN AND CARBON MONOXIDE AT TERRA NOVA BAY (ANTARCTICA)

E. CORAZZA*[#], M. MONTAGNOLI[†] and G. TESI[‡]

** Istituto Geocronologia e Geochimica Isotopica, CNR, Via Maffi 36—56100 Pisa, Italy; [†]Istituto Metodologie Avanzate Inorganiche, CNR, Via Salaria km 29.300—00016 Monterotondo Scalo (Roma), Italy; [‡]Dipartimento di Statistica, Università di Firenze, Viale Morgagni 59—50134 Firenze, Italy*

(Received in final form, 3 August 1993)

During the 1990–91 austral summer atmospheric hydrogen and carbon monoxide were measured on the spot and continuously during one month, near the Terra Nova Italian base in Antarctica. The present work represents the continuation of the previous campaign; the 1990–91 results (H_2 = 522±7 ppbv and CO = 51±1 ppbv) indicate concentrations similar to the ones found in the 1989–90 summer for both components. The sudden hydrogen peaks found in 1989–90 were not found again in 1990–91, confirming the hypothesis that they were local artifacts. CO shows some slow variations as well as a sharp peak (pollution?); yet the concentration dependence on the wind direction (origin of air masses) is not so evident as in 1989–90. The former component represents an even worldwide distribution, while CO represents the present base level for the whole atmosphere, as can be found only in the most remote areas like the southern oceans and Antarctica; this is a consequence of its short residence time in the atmosphere.

KEY WORDS: Carbon monoxide, hydrogen, Antarctic atmosphere, Terra Nova Bay.

INTRODUCTION

The most recent works on CO and H_2 indicate that the role played by trace components cannot be underestimated in the global atmospheric balance; the former component especially is to be followed with a particular care. An accurate knowledge of the distribution of atmospheric carbon monoxide is necessary in order to thoroughly understand the chemistry of the atmosphere. CO plays a key role in tropospheric chemistry: if its concentration increases, CO is likely to increase the average lifetime of other gases like CH_4, a major greenhouse gas, because of its demonstrated covariance with CH_4 and with the OH radical[1]. This implies that CO is likely to have doubled in the last century (as CH_4 did) and acts as a sink for OH, the species which has the advantage of combining with many natural and man-made pollutants. Judging from these peculiar characteristics of CO the concern of atmospheric scientists appears to be justified, in spite of the fact the CO is not a greenhouse

---

[#] To whom correspondence should be addressed.

gas, but instead an ozone producer through photochemical reaction with O_2 [2]. The total balance for CO is positive, with a demonstrated increase due to human activities which account for 60% of the total (burning of biomass and fossil fuels, and hydrocarbon oxidation); the remaining 40% is derived from natural production by hydrocarbon oxidation and by algae and bacteria, mostly planctonic[3]. The same authors estimate a presence of 0.4 Pg (Peta = 10^{15}) in the atmosphere, corresponding to a concentration of 100 ppbv, while the yearly production is on the order of 2.6 Pg. The sinks for CO are its reaction with the OH radical and to a lesser degree its reaction in soils and its diffusion in the stratosphere, with an average lifetime of two months. Because of its covariance with CH_4, its increase also lengthens the lifetime of CH_4 [4]. The knowledge of CO can be considered sufficient for urban areas, but it is generally poor for rural areas regardless of the country; it is definitely scarce for areas with low populations, while only a few observations are available for remote areas, such as open oceans and polar regions.

Hydrogen in the atmosphere is one of the least studied gases; only very few recent studies are available which demonstrate its global variation[5] and its seasonal oscillations, along with a latitude-dependent distribution and an anti-phase correlation with CO [6]. The sources for H_2 are water and formaldehyde dissociation, while its sinks are recombination with O_2 and with the OH radical, as well as diffusion in the stratosphere and in the outer space.

EXPERIMENTAL

The tropospheric trace gases H_2 and CO were determined near the ground (approximately 5m above the ground level) in the proximity of the Italian Antarctic base "Terra Nova Bay"; the instrumentation was housed inside the astronomical observatory OASI, located approximately 0.5 km WNW of the base. Continuous measurements were taken for one month, from Jan 12 to Feb 11, 1991. Measurements were started after having accomplished the other necessary duties of the Environmental Chemistry team (sampling for the homeland laboratories) and after the necessary time for installation and start up. Disassembling and re-packing of the instrumentation for shipment back to Italy were delayed to the last available day. The instrumentation was installed inside a laboratory kindly loaned by the Cosmo-Physics group.

Analyses were carried out in an automated mode according to the above calendar; a period of three hours was chosen as a compromise between safety of control and time coverage. During the month of continuous instrument operation some data were missed because of gaps in the electric supply, and no self-starting procedure was available for the instrument. This represents a simple problem with a difficult solution, because of the random states of relays interfacing the PC and the GC: bi-stable controls need in this case to be interrogated before being restarted, with a resulting complication.

Instrumentation and calibration

The instrumentation used in 1990–91 was very similar to the one used in the previous season [7]; it consisted in a gas-chromatograph self-built by Corazza [8], equipped with an RGD detector which has a high sensitivity for H_2 and CO; the carrier gas was helium, purified from reduced species through a hot catalytic filter (metal oxides) and through an H_2O-CO_2 absorber, yielding sub-ppb pure gas. Automation was obtained through an Olivetti M-10 PC plus custom- and home-built (by Tesi) interfaces controlling three electric valves, the injection valve, the vacuum pump, and the recorder. Using these devices air was sucked from above the laboratory roof for 1 minute to purge the system (the GC was excluded during this step); then the loading section of the GC was also purged for 30 seconds; after completion of the flushing and pressure re-equilibration for 5 seconds with the vacuum pump shut off, the sample was injected. The typical analysis lasted 6 minutes in total; during this period some more timings were controlled. The column was backflushed during the delay time until the next injection. The output was recorded on a strip chart potentiometric recorder; later, peaks were read by a manual method with a sampling period corresponding to 3 seconds. At the time no automatic system for data collection was available; such a lengthy procedure greatly delayed the results. Hydrogen peaks were measured as heights because of their narrow shape.

About 200 measurements were obtained in the automated mode, both for H_2 and for CO. The air samples were calibrated against a standard gas mixture which was run every few days (typically two) at different pressures, in order to obtain a whole range of partial pressures of the standard gases (typically 4–5 each time). The standard gas, purchased as "certified", was actually re-calibrated before and after the campaign in the laboratory in Italy, diluting pure components at the moment with helium controlled at the highest sensitivity and treated in the same way as the carrier gas. Dilutions were made by means of weight-calibrated syringes and glass vials, with a maximum of two dilution steps; this method averages the experimental errors of calibration of the standards and at the same time gives information about the aging of the low concentration mixtures.

All analyses were carried out on site without any sample storage; even though analyses can be performed in this way in only one location, the procedure is preferred when dealing with ppb levels. Sample storage of ppb components is extremely delicate, and particular care is to be devoted to the materials as well, as discussed in a previous paper [7].

Part of the instrumentation used in Antarctica (either commercial and home-built) was ENEA-PNRA property, and was loaned for the most part by the Italian CNR and by Osservatorio Vesuviano (Naples); the remainder was private property (the authors').

Peak integration

The area for the CO peak (both in samples and in standards) was calculated from the hand-digitalized data by means of an appropriate program that calculates the best fitting between the experimental points and a polynomial equation in areas off the peak where visual inspection confirms that they belong to the baseline; peak tailing was taken into account. The degree of the polynomial equation changes automatically (up to the 6th or the 7th, typically the 4th) until a fitting with $R^2>99.9$ is reached. The peaks carrying the greatest integration errors are the very flat ones, where the peak end-points are difficult to recognize. The heights of this curve are then calculated at points corresponding to the experimental ones; the difference between the two series yields a zero-baseline diagram. The peak integration is then obtained as a cubic spline interpolation through the experimental points, and at a variable spacing; the peak area is the total of the sums of all elemental areas obtained by a low pitch interpolation between adjacent experimental points. A test on standard curves demonstrated that the approximations involved are lesser than instrumental errors by and large.

RESULTS AND DISCUSSION

Hydrogen

The relatively long lifetime of hydrogen, of the order of two years, accounts for its almost constant distribution; some latitudinal differences, as well as seasonal oscillations, are measurable and only very recently have been detected [6,9], though not yet completely explained. Until a few years ago this component did not receive any particular attention: the very few articles dealing with H_2 treated it in a simplistic way.

The analytical results, reduced to the standard conditions, are given in Table 1; the average concentration resulted to be 522±7 ppbv, the uncertainty being given as 1.96 times the SE (Standard Error of the arithmetic mean, defined as the Standard Deviation divided by the square root of the number of observations). This value is in agreement with other measurements in Antarctica [5,9], and with 528±25 ppbv found in the 1989–90 campaign [7]. The skewness index (third order moment) is 0.29 and the kurtosis index (fourth order moment) is –0.53; the frequency distribution of concentrations is far from normal, but it follows a bimodal model, as shown in Figure 1.

The frequency distribution of the original data, divided into classes with amplitude equal to 1/4 the S.D. as in Figure 1, exhibits some peaks. In order to understand this irregularity, distributions were compared with theoretical models by means of Kolmogoroff and Smirnoff's test, based on the largest absolute difference between the cumulative frequency distributions of original data and of the hypothesized model. With a statistical significance level of 5% the critical value for 194 observations is:

$$D_{\max} = K_{(\alpha = 0.05)} \sqrt{(2.n)} = 1.36 \sqrt{(2.194)} = 27$$

If the absolute difference between the two cumulative distributions exceeds 27 at least in one point, the two distributions are significantly different. Comparing the H_2 distribution with a normal one, $D_{\max} = 38$. This significant difference suggests that data be represented through a normal distribution overlapped to a binomial one which includes 24% of observations, and with the binomial coefficient $p = 0.91$. This model interprets the bimodality of the distribution (Figure 2), and at the same time allows the inference of an average value of approximately 540 ppbv for the normally distributed data. In view of the present configuration of instrumental measurements and of their manual readings, the binomial fraction of data can be attributed to experimental errors, also because no more reference parameters are available.

The hydrogen peaks found in 1989–90 (and then attributed to local pollution outside the GC system) were not found again during the 1990–91 season, thus confirming the hypothesis

Table 1 Hydrogen and carbon monoxide concentrations, with the sampling time (GMT) and the meteorologic conditions: wind direction, wind speed, pressure. The "—" symbol means data not available.
Sample remarks—40: helicopters & ship; 48, 124, 125, 126: snowing; 86, 87, 88, 89, 90: catabatic wind.

Sample	*Date*	*Time*	*H2*	*CO*	*Wind*		*Pressure*
n.	*(d m y)*	*(h m)*	*ppbv*	*ppbv*	*Dir.*	*Knots*	*(mb)*
1	13 01 91	18 30	553	64	0	1	970.1
2		21 30	548	48	0	2	970.4
3	14 01 91	00 30	525	51	20	5	970.2
4		06 30	539	70	10	5	969.8
5		09 30	532	60	20	3	969.8
6		12 30	567	43	290	7	969.8
7		15 30	—	42	290	15	969.3
8		21 30	541	37	310	12	970.6
9	15 01 91	03 30	555	53	310	14	971.3
10		06 30	605	48	270	10	971.6
11		09 30	591	55	270	10	971.9
12		12 30	576	58	300	9	972.0
13		15 30	—	60	280	18	971.4
14		21 30	585	40	300	10	972.4
15		22 15	598	68	290	8	972.4
16	16 01 91	01 15	596	54	270	7	972.4
17		04 15	605	58	70	5	972.1
18		07 15	630	39	10	5	971.9
19		10 15	608	41	350	2	971.9
20		13 15	599	43	340	1	971.8
21		16 15	607	51	230	2	971.6
22		19 15	590	44	270	5	971.7
23		22 15	596	38	310	7	972.1
24	17 01 91	01 15	586	48	20	6	972.3
25		04 15	564	52	70	4	972.2
26		07 15	576	65	10	3	972.5
27		10 15	588	60	350	2	972.9
28		13 15	577	58	200	5	973.9
29		16 15	572	53	150	7	974.5
30		19 15	568	41	30	4	975.5
31		22 15	568	44	80	4	976.2
32	18 01 91	01 15	592	51	70	6	976.3
33		04 15	552	48	20	4	976.0
34		07 15	560	36	330	4	975.6
35		19 15	653	63	300	2	972.1
36	19 01 91	05 10	576	34	0	5	970.5
37		08 10	575	32	20	2	971.0
38		11 10	563	25	180	9	972.2
39		21 30	538	23	20	3	975.5
40	20 01 91	06 45	575	39	350	3	979.2
41		09 45	548	37	310	14	980.6
42		12 45	568	37	320	24	981.5
43		15 45	546	33	300	19	983.0
44		18 45	572	35	310	15	984.5
45		21 45	547	38	320	11	985.5
46	21 01 91	00 45	570	42	120	6	986.3
47		03 45	548	54	115	9	987.0
48		22 30	513	67	—	—	—
49	22 01 91	01 30	500	48	150	4	984. 8

Table 1 Continued.

Sample n.	*Date (d m y)*	*Time (h m)*	*H2 ppbv*	*CO ppbv*	*Wind Dir.*	*Wind Knots*	*Pressure (mb)*
50		04 30	503	61	—	—	—
51		07 30	513	55	—	—	—
52		10 30	493	53	—	—	—
53		13 30	488	51	—	—	—
54		16 30	—	51	—	—	—
55		19 30	—	51	—	—	—
56		22 30	483	55	—	—	—
57	23 01 91	01 30	528	49	100	2	977.5
58		04 30	551	56	130	4	976.4
59		07 30	558	59	190	4	975.4
60		10 30	543	60	290	3	973.9
61		13 30	528	54	40	2	972.2
62		16 30	—	55	115	4	970.8
63		19 30	—	52	165	12	969.7
64		23 30	499	64	20	4	969.1
65	24 01 91	02 30	514	55	100	3	969.0
66		06 30	565	67	240	24	969.5
67		09 30	534	56	210	17	971.8
68		12 30	539	62	240	6	973.4
69		15 30	545	53	280	21	973.9
70		18 30	533	51	290	14	975.9
71		21 30	542	58	275	12	977.1
72	25 01 91	00 30	588	69	320	19	977.9
73		03 30	546	70	320	12	978.8
74		06 30	670	74	260	15	979.8
75		09 30	—	63	290	19	980.8
76		20 50	540	54	285	30	985.0
77		23 50	544	71	280	25	985.0
78	26 01 91	02 50	511	72	25	8	985.2
79		05 50	522	62	295	11	985.3
80		08 50	531	58	295	39	983.5
81		11 50	494	54	310	32	984.4
82		14 50	—	59	315	30	985.0
83		20 50	448	49	300	33	985.7
84		23 50	463	52	290	38	985.9
85	27 01 91	02 50	472	47	295	36	984.6
86		05 50	480	55	305	37	983.8
87		08 50	461	52	320	55	983.4
88		11 50	458	45	320	50	983.2
89		14 50	437	43	315	41	983.3
90		17 50	427	39	320	41	983.0
91		20 50	458	51	335	18	983.6
92		23 50	449	54	160	3	982.5
93	28 01 91	02 50	489	56	70	3	981.7
94		05 50	532	60	70	6	980.2
95		08 50	523	54	60	5	979.9
96		11 50	499	51	345	7	979.6
97		20 50	466	44	310	8	978.6
98		23 50	476	49	310	15	978.6
99	29 01 91	02 50	482	44	320	16	978.9
100		05 50	476	50	80	5	979.4

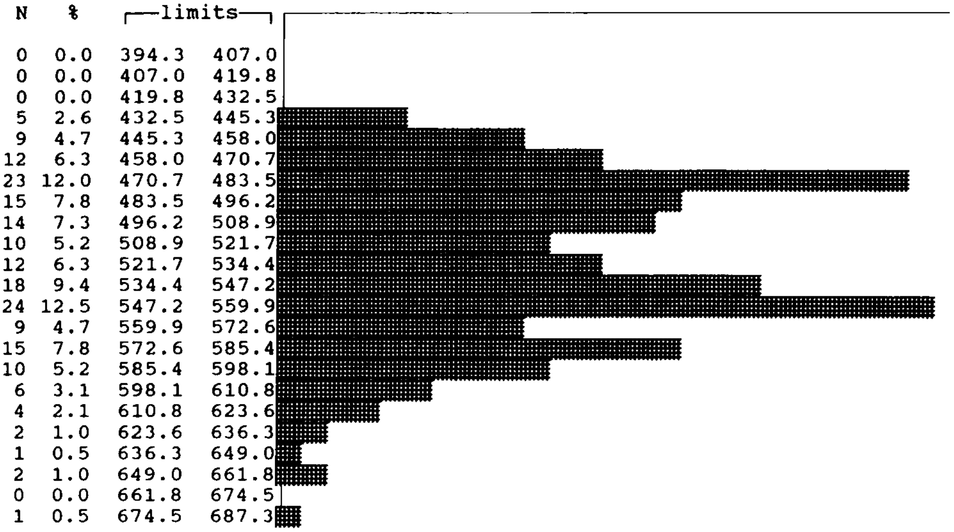
Table 1 Continued.

Sample	*Date*	*Time*	*H2*	*CO*	*Wind*		*Pressure*
n.	*(d m y)*	*(h m)*	*ppbv*	*ppbv*	*Dir.*	*Knots*	*(mb)*
101		08 50	477	53	330	2	979.4
102		11 50	467	42	275	5	979.5
103		14 50	440	49	255	7	979.2
104		17 50	440	37	140	3	978.9
105		20 50	480	45	300	6	979.0
106		23 50	548	70	280	6	978.7
107	30 01 91	02 50	587	68	320	15	977.7
108		05 50	580	77	45	6	976.6
109		08 50	579	77	295	5	975.7
110		11 50	550	53	250	3	975.2
111		14 50	531	57	315	11	974.1
112		17 50	516	48	320	15	974.4
113		20 50	523	53	310	25	974.0
114		23 50	523	47	295	24	974.7
115	31 01 91	02 50	—	96	305	20	975.9
116		05 50	635	127	310	15	977.2
117		08 50	651	122	310	12	979.0
118		11 50	625	83	310	11	980.9
119		14 50	596	71	310	10	982.8
120		20 50	579	72	295	13	986.9
121		23 50	560	61	315	17	987.5
122	01 02 91	02 50	549	63	305	4	989.0
123		05 50	549	59	295	2	990.3
124		08 50	542	58	335	2	991.3
125		11 50	534	57	0	3	992.0
126		20 50	485	50	305	2	992.8
127		23 50	542	64	255	13	992.7
128	02 02 91	02 50	540	57	290	2	992.3
129		05 50	534	60	120	6	992.7
130		08 50	532	54	210	2	992.6
131		11 50	531	54	185	6	992.2
132		14 50	541	60	55	1	992.0
133		17 50	503	54	295	3	991.4
134		20 50	544	56	20	3	990.9
135		23 50	571	71	135	5	990.3
136	03 02 91	02 50	547	57	105	5	989.5
137		05 50	536	58	175	8	988.7
138		08 50	511	48	315	5	988.2
139		11 50	471	45	275	4	987.9
140		14 50	452	41	280	2	987.5
141		17 50	427	36	105	3	987.1
142		20 50	472	29	140	9	987.6
143		23 50	544	76	75	4	988.1
144	04 02 91	02 50	516	50	105	3	988.5
145		05 50	519	56	345	4	989.1
146		08 50	513	56	330	5	989.9
147		11 50	499	46	295	7	990.7
148		14 50	482	40	295	6	991.0
149		17 50	461	45	270	7	991.1
150		20 50	601	—	320	4	991.3
151		23 50	499	52	320	6	991.2

Table 1 Continued.

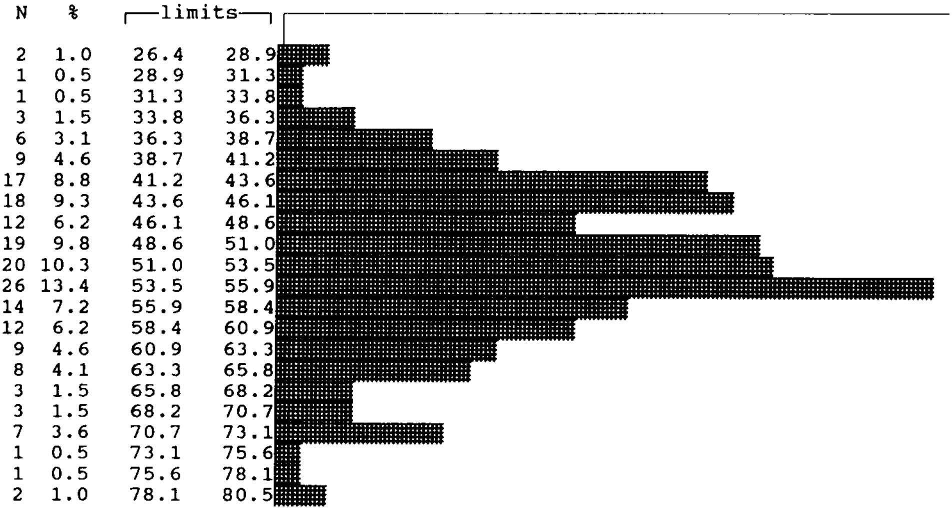
Sample	*Date*	*Time*	*H2*	*CO*	*Wind*		*Pressure*
n.	*(d m y)*	*(h m)*	*ppbv*	*ppbv*	*Dir.*	*Knots*	*(mb)*
152	05 02 91	02 50	521	53	15	3	990.8
153		05 50	556	71	15	5	990.3
154		08 50	533	55	325	3	990.1
155		11 50	518	42	275	4	989.9
156		14 50	502	46	115	3	989.5
157		17 50	497	55	175	6	989.2
158		20 50	523	50	100	3	989.1
159		23 50	554	64	130	5	988.6
160	06 02 91	02 50	511	49	355	5	987.5
161		05 50	504	57	340	3	986.1
162		08 50	490	54	230	5	984.8
163		11 50	488	42	280	4	983.9
164		14 50	480	42	195	2	982.7
165		17 50	474	43	115	5	981.5
166		20 50	474	43	295	5	980.5
167		23 50	488	50	65	2	979.9
168	07 02 91	02 50	470	47	70	4	979.5
169		05 50	471	41	25	3	979.4
170		08 50	469	45	285	5	979.8
171		11 50	447	45	305	3	980.1
172		14 50	446	41	70	4	980.7
173		17 50	437	40	215	4	981.6
174		20 50	442	39	315	27	983.2
175		23 50	457	44	330	7	985.4
176	08 02 91	02 50	469	50	290	30	988.0
177		05 50	475	43	45	8	990.6
178		08 50	472	44	175	4	992.6
179		11 50	455	39	10	5	994.1
180		14 50	452	41	5	4	995.1
181		17 50	438	42	350	3	995.9
182		20 50	441	44	50	4	996.0
183		23 50	456	41	10	4	995.0
184	09 02 91	02 50	475	51	30	4	993.6
185		05 50	481	51	330	23	992.0
186		06 20	503	54	315	24	990.6
187		06 30	493	50	300	23	990.7
188		08 50	474	49	310	34	990.2
189		11 50	473	45	295	40	988.5
190		14 50	474	42	300	45	987.3
191		17 50	479	51	295	69	984.1
192		20 50	491	51	300	32	986.3
193		23 50	492	49	310	24	988.2
194	10 02 91	02 50	478	52	290	41	987.7
195		05 50	473	46	265	18	988.7
196		08 50	460	43	85	3	989.6
197		11 50	454	49	295	9	989.9
198		14 50	450	43	270	40	989.1
199		17 50	475	41	230	15	988.6
200		20 50	473	45	5	4	989.2
201		23 50	481	46	325	2	989.2

```
   N      MEAN       S.D.      ASYMMETRY  KURTOSIS
  192. 521.67820  50.94809   0.29452   -0.53006
  Min =426.60 Max=669.90
  Q1=476.52 Median =523.00 Q3=554.92   78.40 Q3-Q1=
  Median Absolute Deviation =  42.25
```



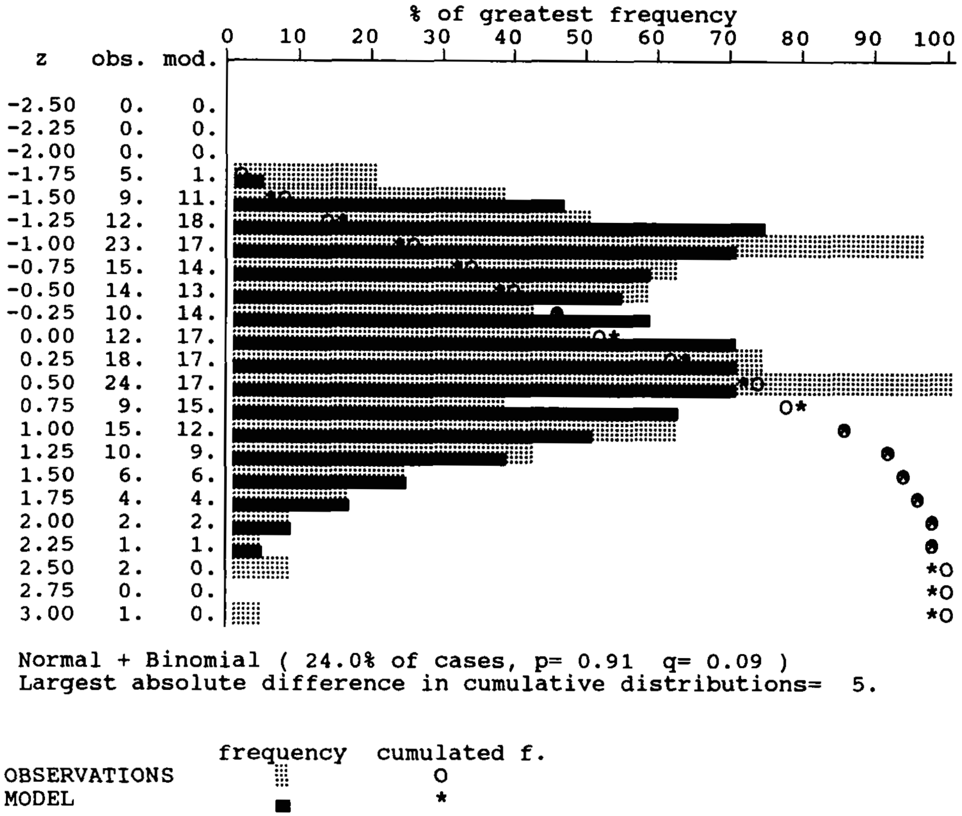
```
 N   %     ┌──limits──┐
 0  0.0   394.3   407.0
 0  0.0   407.0   419.8
 0  0.0   419.8   432.5
 5  2.6   432.5   445.3
 9  4.7   445.3   458.0
12  6.3   458.0   470.7
23 12.0   470.7   483.5
15  7.8   483.5   496.2
14  7.3   496.2   508.9
10  5.2   508.9   521.7
12  6.3   521.7   534.4
18  9.4   534.4   547.2
24 12.5   547.2   559.9
 9  4.7   559.9   572.6
15  7.8   572.6   585.4
10  5.2   585.4   598.1
 6  3.1   598.1   610.8
 4  2.1   610.8   623.6
 2  1.0   623.6   636.3
 1  0.5   636.3   649.0
 2  1.0   649.0   661.8
 0  0.0   661.8   674.5
 1  0.5   674.5   687.3
```

```
  N      MEAN       S.D.      ASYMMETRY  KURTOSIS
 194.  51.01287   9.83822   0.22643    0.19496
 Min = 22.60 Max= 77.40
 Q1= 43.58 Median = 50.90 Q3= 56.88   13.30 Q3-Q1=
 Median Absolute Deviation =   6.60
```



```
 N   %      ┌──limits──┐
 2  1.0    26.4    28.9
 1  0.5    28.9    31.3
 1  0.5    31.3    33.8
 3  1.5    33.8    36.3
 6  3.1    36.3    38.7
 9  4.6    38.7    41.2
17  8.8    41.2    43.6
18  9.3    43.6    46.1
12  6.2    46.1    48.6
19  9.8    48.6    51.0
20 10.3    51.0    53.5
26 13.4    53.5    55.9
14  7.2    55.9    58.4
12  6.2    58.4    60.9
 9  4.6    60.9    63.3
 8  4.1    63.3    65.8
 3  1.5    65.8    68.2
 3  1.5    68.2    70.7
 7  3.6    70.7    73.1
 1  0.5    73.1    75.6
 1  0.5    75.6    78.1
 2  1.0    78.1    80.5
```

Figure 1 Frequency distribution of H_2 (top) and CO (bottom) concentrations (ppbv). For hydrogen all data are included; for carbon monoxide the peak on Jan 31 was ruled out. Some statistical indices are given in the headings (see text); "limits" = ppbv.



```
  z     obs.  mod.
-2.50    0.    0.
-2.25    0.    0.
-2.00    0.    0.
-1.75    5.    1.
-1.50    9.   11.
-1.25   12.   18.
-1.00   23.   17.
-0.75   15.   14.
-0.50   14.   13.
-0.25   10.   14.
 0.00   12.   17.
 0.25   18.   17.
 0.50   24.   17.
 0.75    9.   15.
 1.00   15.   12.
 1.25   10.    9.
 1.50    6.    6.
 1.75    4.    4.
 2.00    2.    2.
 2.25    1.    1.
 2.50    2.    0.
 2.75    0.    0.
 3.00    1.    0.

Normal + Binomial ( 24.0% of cases, p= 0.91  q= 0.09 )
Largest absolute difference in cumulative distributions=  5.

                  frequency  cumulated f.
OBSERVATIONS          ▨          O
MODEL                 ■          *
```

Figure 2 Frequency distribution of H_2 concentrations in Standard Units:
Z score = (value-mean)/Standard Deviation
The observations are compared with models (normal plus binomial). The quality of similarities is evaluated with the "Largest absolute difference in cumulative distributions".

of artifacts. Because of this all the 1990–91 hydrogen data were treated together without rejecting any values. In Figure 4 the H_2 relationships with wind direction (reduced to octants) and with wind speed (reduced to three classes) are shown; it appears evident that H_2 is totally independent of wind conditions. In the present analysis, wind speed and direction are limited to one set of data only for each analysis; data are chosen as close as possible to the moment of injection. For the continuation of this work it will be useful also to consider the wind parameters in different moments prior to the sampling time, in order to reconstruct the history of air masses.

The high diffusion coefficient of hydrogen, coupled with its relatively long lifetime, is responsible for its uniform worldwide distribution, in a way similar to that of CO_2. The seasonal oscillations in phase between the two hemispheres have yet to be understood; tentatively they have been attributed to the asymmetric distribution of the continents[5].

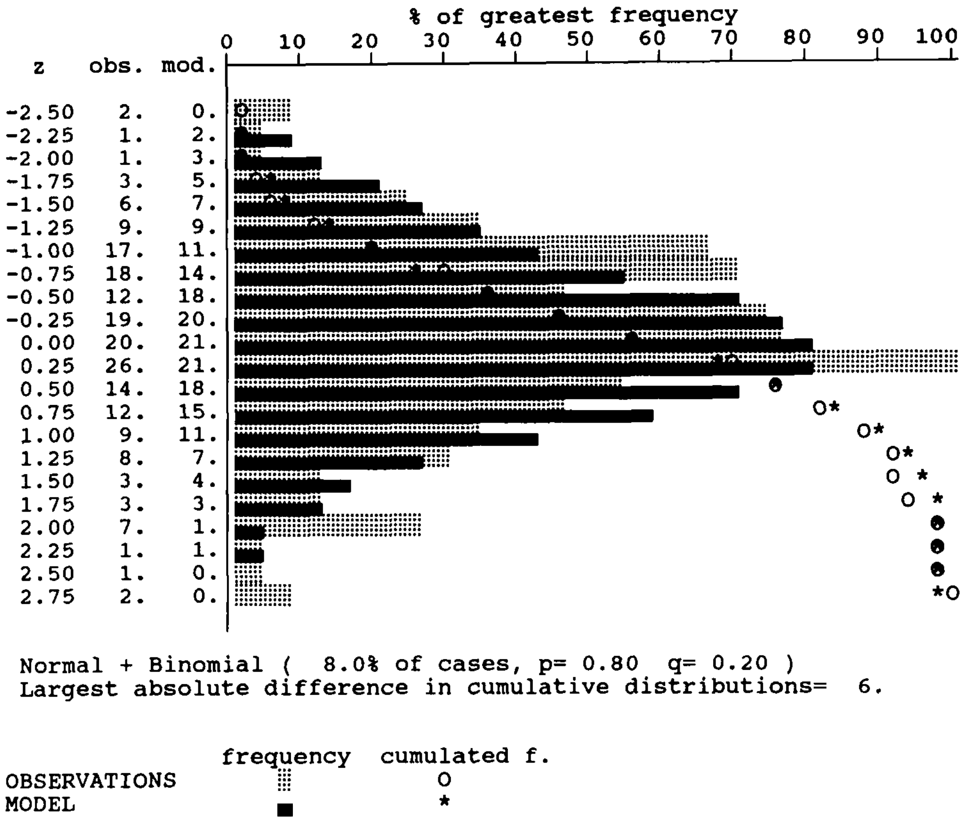


Figure 3 Frequency distribution of CO concentrations in Standard Units (same as in Figure 2).

Carbon monoxide

Carbon monoxide has received greater attention by most authors because of its importance in global cycles, as outlined in the introductory chapter.

Some of the samples are polluted from human activities at the base or in the surroundings of the OASI observatory, as demonstrated in the 1989–90 campaign; a CO peak of the duration of a whole day was found on Jan 31, 1991: a rapid increase is evident, with a long tailing decrease. During this burst the wind direction remained almost constant at around 310°, and the wind speed ranged between 10 and 20 knots. The origin of this peak cannot be explained as yet; it might be local pollution (the ship at Tethys Bay?), but the available information is insufficient for making a definite affirmation.

The overall mean concentration of CO was found to be 52±2 ppbv; it decreases to 51±1 ppbv ruling out the "anomalous" peak. The skewness index passes from 1.98 to 0.19, and the kurtosis index from 8.85 to 0.19, respectively, while the median value remains at around 51 ppbv in both cases. That is, in the case of peak rejection, the distribution of CO concentrations results to be almost normal, as can be seen in Figure 1.

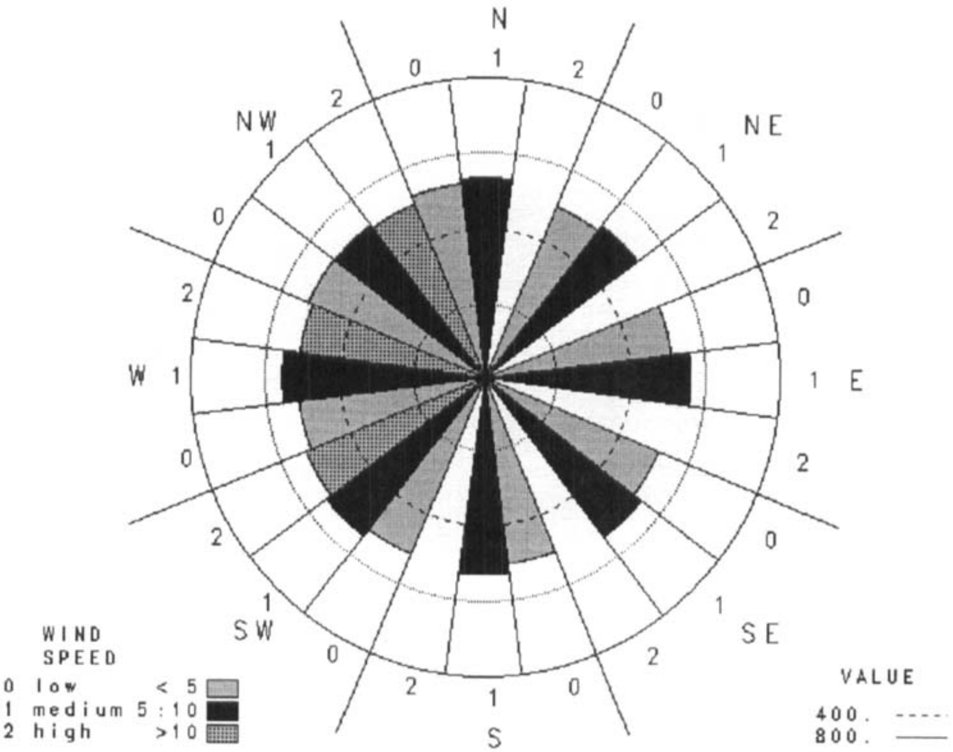


Figure 4 Wind categories *versus* hydrogen concentrations. The wind speed categories (knots) are resulting from an overall analysis of all data. The radius of each sector represents the concentrations; the radius steps are of 200 ppbv. Wind directions are divided into octants. The gaps in the diagram represent wind speed categories not recorded.

On the other hand, the CO dependence on the wind direction, interpreted as an indication of different origins of air masses, and clearly evident from the results of 1989–90, is not as clear in the 1990–91 campaign. The westerlies yielded 51±2 ppbv CO in the former instance, against 63±8 from the other quadrants; in the second case there is no actual difference among the quadrants: 51±2 ppbv in either case, taking into account the approximations. The reason for this different distribution from one year to the next can be attributed to different weather conditions, resulting from different seasonal circulations within and around Antarctica. The average concentrations found for the air masses associated with winds from the Ross Sea, or in close proximity, resemble the ones from the W quadrant (winds from the inland ice plateau) in 1990–91, as well as the ones of this same quadrant for the 1989–90 season, as if the unchanged air masses did not meet any main source of CO. In Figure 5 the CO concentrations are plotted against wind speeds (divided into three classes) and against wind directions. Again, the almost constant concentration of CO is confirmed, as well as a non-dependence on the wind speed; inclusion of the peak on Jan 31 only enhances the triangle representing medium winds from the SW quadrant.

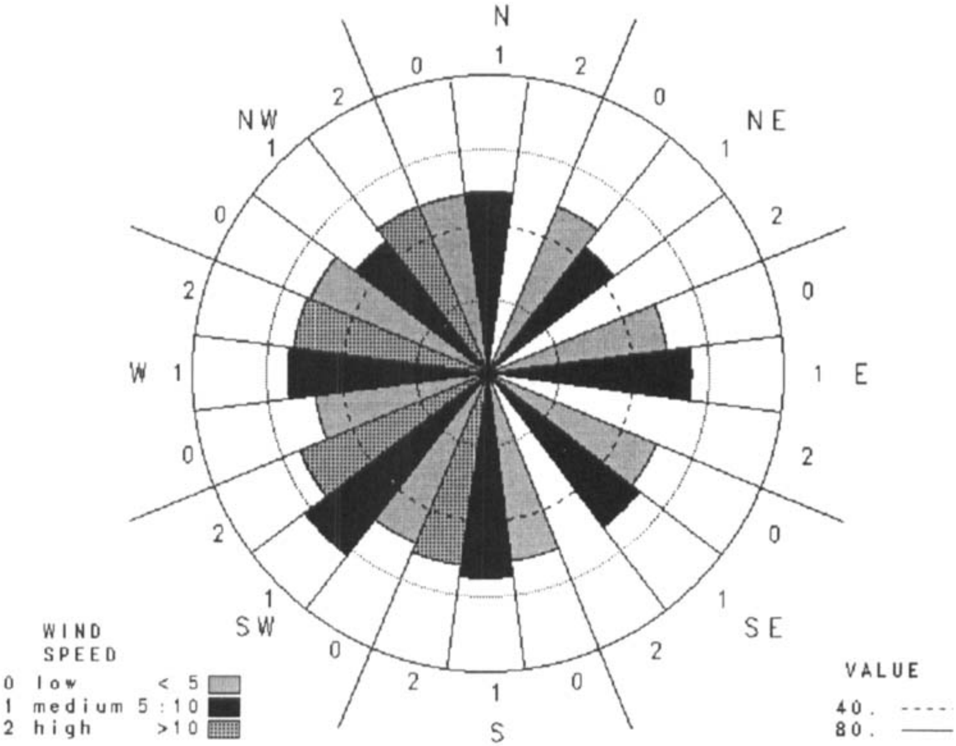


Figure 5 Wind categories *versus* carbon monoxide concentrations. The radius steps are of 20 ppbv. The remaining features as in Figure 4.

The interpretation of the original data for CO (Figure 1), evaluated as Z scores and given in Figure 2, shows a slight difference from a normal distribution: $D_{max} = 16$. This value, though below the statistical significance level, is still appreciable. The insignificant asymmetry found in CO distribution can be accounted for by combining the normal model with a bimodal one which includes only 8% of observations. In this case, it is the neutralization of a peak including a few low values lying one S.D. below the average. In this distribution a tailing of high values (more than 2 S.D.'s above the average) is also present; the normal distribution is not significantly modified by these data. Also in the case of CO, the deviations from the normal distribution are physically interpreted as instrumental errors, which can only be reduced with a more advanced method of data acquisition and peak measurement.

The average concentration calculated for the 1990–91 campaign and the concentration found in the previous season for the westerlies are comparable to the ones found in such remote areas as the southern Pacific[10], and when flying above Antarctica itself[11]; only at the South Pole Clean Air Sector a lower CO concentration (40 ppbv) in 1986 and 1987 for the same season was found[3,5]. In the Antarctic Peninsula (Palmer) it was found to be higher[12,13].

The study of CO in remote areas such as Antarctica is of paramount interest in establishing the present background situation which already includes the man-induced variation of the industrial period. The results (namely the concentrations associated with continental air masses) represent the Antarctic background; this is to be regarded as the present background for the whole atmosphere, most of the artificial CO being produced in the northern hemisphere. This is one of the bases for the understanding of atmospheric circulation and of global changes induced by anthropic modifications.

Acknowledgements

Many thanks are due to Dr. G. Dall'Oglio and his team of the Cosmo-Physics sector of the VI Italian expedition, for their hospitality in the OASI observatory and for their help. The authors are also indebted to the ENEA Meteorology Group (Drs. L. De Silvestri, P. Grigioni, and A. Pellegrini) for weather information.

This study was financed in the framework of the Italian National Programme for Antarctic Research (PNRA).

References

1. P. D. Guthrie, *Global Biogeochemical Cycles*, **3**, 287–298 (1989).
2. S. E. Schwartz, *Nature*, **343**, 209–210 (1990).
3. M. A. K. Khalil and R. A. Rasmussen, *Chemosphere*, **20**, 227–242 (1990).
4. D. A. Lashof and D. R. Ahuja, *Nature*, **344**, 529–531 (1990).
5. M. A. K. Khalil and R. A. Rasmussen, *Antarctic J. of the U.S.*, **24**, 238–239 (1989).
6. M. A. K. Khalil and R. A. Rasmussen, *Tellus*, **41B**, 554–559 (1989).
7. E. Corazza and G. Tesi, *Ann. Chim. (Rome)*, **81**, 439–451 (1991).
8. E. Corazza, Italian Patent 9474 A/89 (1989).
9. M. A. K. Khalil and R. A. Rasmussen, *Nature*, **347**, 743–745 (1990).
10. K. C. Kelly-Hansen, *Eos*, **68**, 1220 (1987).
11. R. Pratt and P. Falconer, *J. Geophys. Res.*, **84**, 7876–7882 (1979).
12. M. A. K. Khalil and R. A. Rasmussen, *Nature*, **332**, 242–245 (1988).
13. D. R. Cronn and K. J. Schilling, *Reviews of Geophysics*, **26**, 497–518 (1988).