A correction for the effect of drying of air samples and its significance to the interpretation of atmospheric CO_2 measurements

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ABSTRACT

Non-dispersive infrared gas analysers used for the measurement of atmospheric carbon dioxide concentration are influenced by water vapour in the air sample. It has thus become common practice to dry the air prior to analysis. The subsequent measurement must be corrected by multiplying the indicated concentration by $(1 + 1.61r)^{-1}$, where r is the water vapour mass mixing ratio of the undried air. The correction is of the order 1 % near the surface, varying in both space (e.g. with latitude) and time (e.g. day-to-day and seasonally), and of the same order of magnitude as the measured but uncorrected horizontal, vertical and seasonal CO_2 variations. Thus serious doubt is thrown on previous comparisons of global CO_2 measurements. Ideally each CO_2 analysis of an air sample should be corrected using knowledge of the water vapour concentration of the undried air. For data obtained in the past, appropriate correction may be possible after consideration of the water vapour conditions in the atmosphere at each of the monitoring stations. This should be done by the research personnel involved with each monitoring programme, together with a consideration of the effects of carrier gas composition on the gas analyser(s) employed.

1. Introduction

During the past 17 years high quality measurements of atmospheric carbon dioxide concentration have been made at several monitoring locations (Table 1), and which indicate a global increase in concentration at a rate of about 0.2 % per annum.

The measurements are believed to have an absolute accuracy of ±0.5 parts per million by volume (ppmv) since they all refer to standard CO_2/N_2 gas mixtures provided by the Scripps Institute of Oceanography. At each station a relative accuracy of ±0.2 ppmv is usually obtained. However valid comparison of the data from all stations is open to two main criticisms.

Firstly it has been shown independently by Bischof (1973) and Pearman & Garratt (1974) that non-dispersive infrared (NDIR) gas analysers can over- or under-estimate CO_2 concentrations by several ppmv when the oxygen/nitrogen ratio in the sample air differs from that of the reference gas mixtures. The sign and magnitude of this "error" also depends on the make of the NDIR analyser used.

Secondly, it has been the practice of research workers to dry air prior to measurement because of the sensitivity of NDIR analysers to water vapour. However the effect of this drying on the indicated CO_2 concentration appears to be generally overlooked in the literature. In this paper I shall indicate the magnitude of the correction to be applied and demonstrate its importance in the interpretation of the global data.

2. The effect of drying

The sensitivity of NDIR analysers to the presence of water vapour has led to the practice of drying the air prior to analysis for CO_2 (see Table 1). However removal of water vapour

Table 1. *Major baseline atmospheric carbon dioxide monitoring stations with details of the NDIR gas analysers and drying procedures used*

Monitoring station	Altitude at which analysis is made	Type of measurement	Type of analyser	Drying procedure	Publication with description of method
Antarctica	Sea level (flask samples analysed at Scripps Inst.)	Flask (1957+)	A.P.[a]	−78°C, dry ice trap	Keeling et al. (1968)
	2.8 km (continuous)	Continuous (1960–63)			Keeling et al. (1972*a*)
Australia	Sea level	Flask	UNOR 2[b] URAS 2	−78°C, dry ice trap or magnesium perchlorate chemical drying. No drying above approx. 8 km	Pearman and Garratt (1973)
Barrow, Alaska	~200 m	Continuous	LIRA 200	−48°C, freezer cell	Kelley (1964)
Makara, N. Z.	Sea level	Continuous	URAS 1	approx. −40°C freon freezer	Lowe (1972)
Mauna Loa, Hawaii	3.4 km	Continuous	A.P.	−78°C, dry ice trap	Pales and Keeling (1965) Keeling et al. (1972*b*)
North atlantic	Sea level	Flask	URAS (modified) Grubb Parsons IRGA 1 and 2 UNOR 2, 5B	−78°C, dry ice trap. No drying of upper air samples	Bischof (1970)

[a] In several publications of the Scripps Institute group, reference is made to analysers of the type described by Smith (1953). Mr P. Guenther (personal communication) indicated that the analysers were by a company no longer operating called Applied Physics. Thus the use of the abbreviation A.P.

[b] Data collected using the UNOR 2 are adjusted to be consistent with what would be indicated by a URAS2 analyser, using the relationships published in Pearman & Garratt (1974).

from the air with subsequent restoration to ambient atmospheric pressure causes a concomitant increase in the density of the other components in the air.

To correct for this, indicated CO_2 concentrations should be multiplied by a factor ε which is defined as,

$$\varepsilon = \frac{p_{c1}}{p_{c2}}$$

where p_{c1} and p_{c2} are the partial pressures of CO_2 before and after drying. From Dalton's Law of Partial Pressures,

$$\varepsilon = \frac{p_{a1} + p_{c1}}{p_{a1} + p_{c1} + p_{w1}} = \left(1 + \frac{p_{w1}}{p_{a1} + p_{c1}}\right)^{-1}$$

where p_{w1} and p_{a1} are the original partial pressures of water vapour and air (oxygen and nitrogen) respectively. However,

$$p_{c1} < p_a$$

and from the Ideal Gas Equation

$$\frac{p_{w1}}{p_{a1}} = \frac{\varrho_{w1}}{\varrho_{a1}} \frac{M_a}{M_w}$$

where ϱ_{w1}/ϱ_a is the ratio of the densities of water vapour and air (i.e. the mass mixing ratio, r), and M_a/M_w is the ratio of the molecular weights of air and water vapour ($=1.61$). Therefore,

$$\varepsilon = (1 + 1.61r)^{-1}$$

In table 2 the correction, expressed as a percentage is estimated for a range of ambient

Table 2. *Percentage error in indicated CO_2 under a range of pressure and drying conditions, due to the volumetric effect of drying*

Saturated water vapour conditions are assumed and the table is derived from data given in the Smithsonian Meteorological Tables (1951).

Temperature (0°C)	Pressure (mb) 1 000	850	700	500
−40	0.02	0.02	0.03	0.04
−20	0.13	0.15	0.18	0.25
0	0.61	0.72	0.88	
+20	2.35	2.76		
+40	7.42			

temperature and pressure conditions assuming water vapour saturation. Water vapour mixing ratios were obtained from the Smithsonian Meteorological Tables (1951). Table 2 demonstrates that for realistic ambient conditions, errors of more than 1% are probable if correction for drying is neglected.

As a further illustration, in Table 3 I have used estimates of the mean mid-latitude vertical distribution of water vapour to determine ε and then estimated the error in ppmv of CO_2 assuming a back-ground concentration of 325 ppmv. The table shows that near the earth's surface CO_2 concentrations will be over-estimated by about 3 ppmv due to drying. The error decreases with altitude to be less than the resolution of the NDIR analysers (approximately ±0.2 ppmv) above about 8 km.

3. Interpretation of global-scale CO_2 measurements

Table 1 indicates the methods used for drying of the air prior to CO_2 analysis and the type of NDIR analysers used at the main monitoring stations. To assess the magnitude of the effect of drying on the measurements made at each station, radiosonde data for the years 1971 and 1972 were examined for locations near the monitoring stations (Monthly Climatic Data of the World, 1972; Meteorological Observations for 1971). From the radiosonde water vapour measurements the seasonal variation in the over-estimate of CO_2 concentration was thus determined and plotted in Fig. 1.

These curves can serve only as an indication of the magnitude of the over-estimate due to drying in the absence of information on the water vapour concentrations relating to individual CO_2 data for each monitoring station.

The northern-most station at Barrow, Alaska, situated at 200 m above mean sea level, shows a distinct seasonal cycle with an indicated average over-estimate of about 1 ppmv.

Radiosonde data at the 700 mb level above the town of Hilo (60 km from the station) were considered to be representative of the Mauna Loa station and show little seasonal variation in the water vapour concentration. For the whole year the indicated over-estimate is similar to that at Barrow, viz 1 ppmv.

The water vapour concentrations at the South Pole are sufficiently low throughout the year for the water vapour correction to be negligible. This contrasts with the Makara station in New Zealand where we find an over-estimate for the whole year close to 4 ppmv.

In the Australian monitoring programme air samples are collected over southern Australia, Bass Strait, Tasman Sea and the Southern Ocean south to the South Pole. A significant fraction of these are collected above 8–10 km (as are the Swedish data) where drying is not required. The remainder are obtained at 3.5–5

Table 3. *The annual mean conditions for mid-latitude atmosphere, together with the estimated correction factor required if drying of air precedes the determination of CO_2 content*

An approximate error in ppmv is included assuming a uniform atmospheric CO_2 content of 325 ppmv. Based on data from Handbook of Geophysics and Space Environments (1965)

Geo-potential altitude [km]	Temperature [°C]	Typical H_2O Mass mixing ratio r [ppmm]	Correction factor ε	Approximate error in CO_2 concentration [ppmv]
0	+15	6 300	.98996	3.26
2	+ 2	3 800	.99392	1.98
4	−11	1 900	.99695	0.99
6	−24	900	.99855	0.47
8	−37	270	.99957	0.14
10	−50	37	.99994	0.02
12	−57	17	.99997	0.01

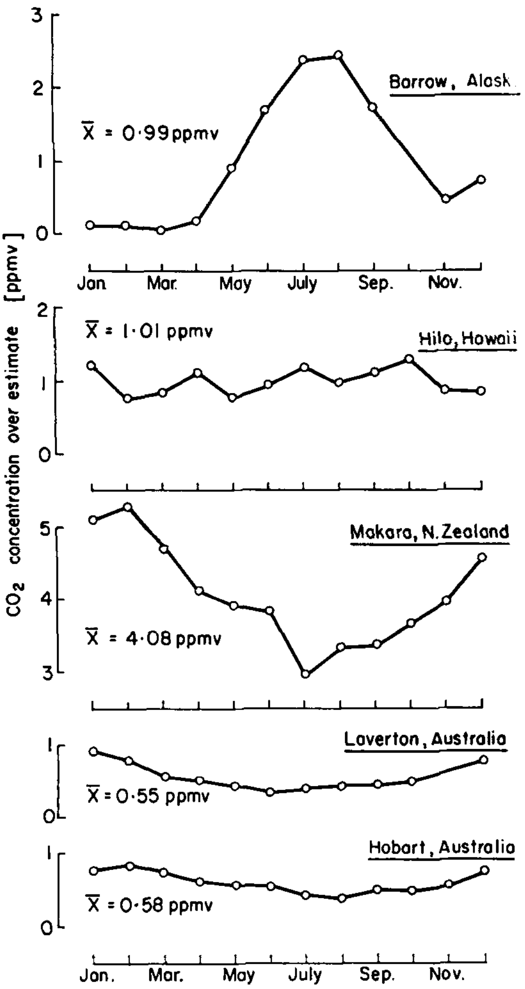

Fig. 1. Estimated seasonal variation in the over-estimate to CO_2 measurements due to the pre-drying effect, at selected Monitoring Locations. Error expressed in ppmv, assuming a background concentration of 325 ppmv, $\bar{X}$ is the annual mean error.

Details of radiosonde sites:

Station	Latitude	Longitude	Elevation	Time of water vapour meas. (hr GMT)
Barrow, Alaska	71°18′ N	156°47′ W	4 m	1 200
Hilo, Hawaii	19°43′ N	155°04′ W	~3.2 km (700 mb)	1 200
Makara, New Zealand	41°15′ S	174°42′ E	297 m	2 100
Laverton, Australia	37°52′ S	144°45′ E	3.1–5.7 km (mean of 500 and 700 mb)	Unknown
Hobart, Australia	42°50′ S	147°30′ E	3–5.6 km (mean of 500 and 750 mb)	Unknown

km where drying is necessary. For the latter set of data, use of radiosonde data for Laverton (near Melbourne) and Hobart (Tasmania) gives an over-estimate of 0.6 ppmv on average.

It is of interest to illustrate the significance of this over-estimate for the Australian data. In Fig. 2, the solid curve shows the vertical distribution of CO_2 based on 6 months of data and previously published by Pearman & Garratt (1973*a*). The figure also shows the profile after correction for the mean water vapour concentration for that time of the year at each altitude. Above about 3 km where the profile is well developed and indicative of the large-

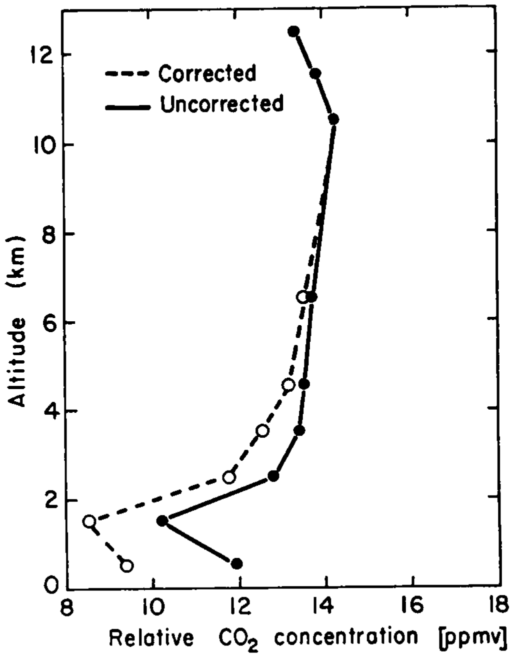

Fig. 2. Carbon dioxide concentrations in the southern hemisphere troposphere relative to a primary reference gas, as a function of height, with and without correction for the pre-drying effect. See original publication for further details. Pearman & Garratt (1973*a*).

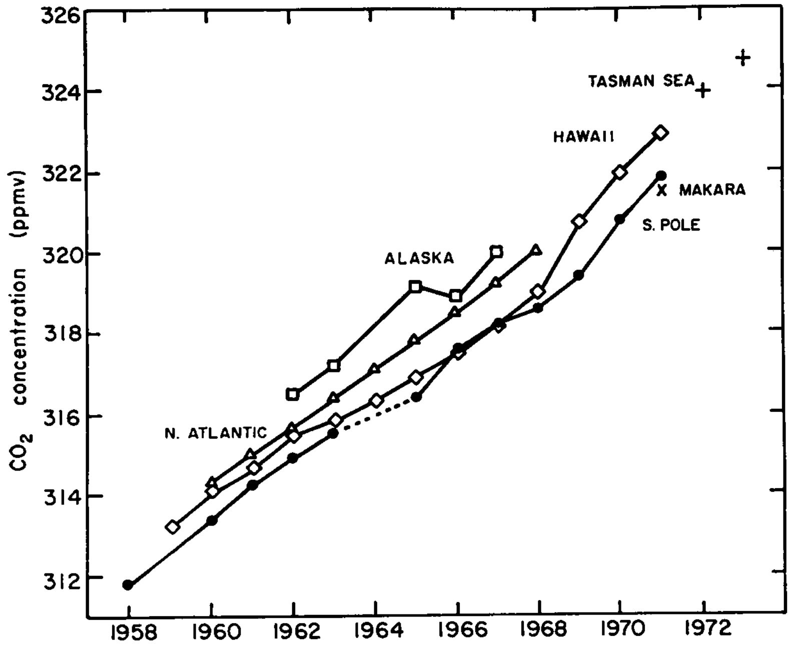

Fig. 3. Trends in atmospheric CO_2 concentration as measured at several monitoring stations. All data relative to the 1969 manometric scale. Sources: Antarctica, Brown & Keeling (1965), Keeling (personal communication), Keeling et al. (1972*a*), note that data are for continuous and flask sampling (○) techniques; Mauna Loa (◇), Keeling et al. (1972*b*); North Atlantic (△), Bolin & Bischof (1970); Barrow (□), Kelley (1969), Bass Strait (+), author's own data; Makara, N. Zealand (×), Lowe (1973).

scale vertical exchange of CO_2, the correction increases the magnitude of the vertical gradient by a factor of two. This is important in the context of the seasonal variations in the large-scale atmosphere-ocean CO_2 exchange discussed by Garratt & Pearman (1973). After correction the seasonal variation in vertical gradient is still evident and can be considered to be related to ocean surface temperature variations. However the vertical gradient in the troposphere at 40° S now indicates a permanent surface sink in the mid latitude oceans of the southern hemisphere equivalent in magnitude to about half the annual CO_2 production from fossil fuel combustion. Perhaps not surprisingly the relatively large correction for the Makara data implies low CO_2 concentrations near the surface, also indicative of an oceanic sink.

Finally, comparison of the data for Mauna Loa and Antarctica which use identical analysers is not strictly valid if large-scale horizontal CO_2 *differences in the atmosphere are to* be interpreted correctly. This arises because, (*a*) no correction is available for the effect of altitude differences (Pearman & Garratt, 1974), (*b*) Drying at Mauna Loa will over-estimate CO_2 concentrations by some 1 ppmv relative to the South Pole, all else being equal. It is therefore somewhat disturbing to find in Fig. 3 that uncorrected CO_2 concentrations at Mauna Loa are about 1 ppmv higher than at the South Pole.

4. Conclusions

CO_2 measurements require correction due to the effect of drying the air sample prior to analysis. At a majority of the monitoring stations data may be sufficiently affected to make valid interpretation and comparison with other stations impossible. Knowledge of the water vapour concentration is required before true CO_2 concentrations can be inferred.

Correction of CO_2 data collected in the past may be possible and should be done by personnel involved in each programme.

Both the carrier gas and the drying problems have wide implications in the interpretation of certain biological experiments involving the measurement of CO_2 by NDIR analysers. These are to be discussed elsewhere.

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ПОПРАВКА НА ЭФФЕКТ ВЫСУШИВАНИЯ ПРОБ ВОЗДУХА И ЕЕ ЗНАЧЕНИЕ ДЛЯ ИНТЕРПРЕТАЦИИ ИЗМЕРЕНИЙ CO_2 В АТМОСФЕРЕ

Недисперсионные инфракрасные газоанализаторы, используемые для измерений концентрации углекислого газа в атмосфере, подвержены влиянию паров воды в пробе воздуха. Поэтому сталц обычной практикой высушивать воздух до проведения анализа. Результаты подобных измерений должны быть подправлены умножением получаемой концентрации на $(1 + 1{,}61r)^{-1}$, где r — отношение смеси водяного пара невысушенного воздуха. Эта поправка порядка 1 % вблизи поверхности земли, меняясь как в пространстве (например, с широтой), так и во времени (например, ото дня ко дню и с сезоном), и того же порядка величины, как измеренные, но не скорректированные вариации CO_2 по горизонтали, вертикали и с сезоном. Таким образом, бросается серьезное сомнение на результаты предыдущих сравнений глобальных измерений CO_2. В идеале, каждый анализ на концентрацию CO_2 в пробе воздуха должен быть подправлен, если известна концентрация водяного пара в невысушенном воздухе. Для данных, полученных в прошлом, соответствующая поправка может быть определена, если известна влажность на каждой из патрульных станций. Это следует сделать исследователям, связанным с каждой патрульной программой, с учетом эффектов несущего газа на показания используемого анализатора.