19TH CENTURY MEASUREMENTS OF ATMOSPHERIC CO_2 – A COMMENT

In a recent paper in this journal, Wigley (1983) has reviewed measurements of the atmospheric CO_2 concentration performed by a French group a century ago on air samples from the northern and southern hemisphere, which were of high standard as to the experimental methods used (Müntz and Aubin, 1886). Müntz and Aubin reported a mean value of 266 ppm for several southern hemisphere series, and of 282 ppm for several series from northern hemisphere stations remote from urban influence. The difference between the hemispheres is clearly significant and much larger than can reasonably be considered real, as pointed out by Wigley. Arguing that contamination by anthropogenic CO_2 is less probable for southern hemisphere air, Wigley suggests that these data point to a value of 260 to 270 ppm for the early 1880s.

However, there is reason to suspect that the southern hemisphere results of Müntz and Aubin may have been systematically too low. They used the method to absorb the CO_2 of a measured air volume on a carbonate-free solution of potassium hydroxide, extracted the CO_2 in the laboratory with sulfuric acid and determined its amount volumetrically. The KOH solution was stored in glass tubes, containing pumice to increase the absorbing surface, which were sealed before and after the absorption. Experience in the Institute for Environmental Physics, Heidelberg (K.O. Münnich, personal communication) has indicated that after prolonged storage in glass, recovery of CO_2 from an alkaline solution may be considerably below 100%. Glass, especially soft glass (which was probably used by Müntz and Aubin), is attacked by alkaline medium, by which some residue is formed. This residue may interfere with the acid-carbonate reaction such that carbon dioxide development is impeded; the phenomenon has not been studied in detail to my knowledge. A similar effect was observed by Letts and Blake (1900) who determined CO_2 concentrations by titration of the alkaline absorbent, and who found it necessary to coat the inner walls of their glass vessels with paraffin. The southern hemisphere samples of Müntz and Aubin must have been stored for many months before CO_2 extraction could be performed in the laboratory, and it seems plausible that sample integrity may have suffered, leading to incomplete liberation of CO_2, that is to too low results. This suspicion is strengthened by definitely too low results of Müntz and Lainé (1911) who obtained a mean value of 205 ppm, with much scatter, for samples collected in Antarctic regions between 64 and 70° S, using a method similar (but not identical) to that of Müntz and Aubin (1886).

Müntz and Aubin also carried out measurements in the Plaine de Vincennes (France), an open field "far from any intensive source of CO_2" but naturally in the vegetation zone, and on the top of Pic du Midi in the Pyrenees. Wigley discards these results because of possible urban influence. This reservation may apply for Plaine de Vincennes, but hardly for Pic du Midi, at 2877 m altitude, remote from urban and from direct vegetational influence. There the following mean values (± 1 standard deviation) were obtained:

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August 1881, 14 samples: 286 ± 9 ppm;
August 1882, 5 samples: 285 ± 16 ppm;
August 1883, 19 samples: 267 ± 9 ppm.

The overall mean is 276 ± 15 ppm. For Plaine de Vincennes, the mean of all 35 samples taken between May and October 1881 is 284 ± 13 ppm, or 280 ± 8 ppm if 4 suspiciously high (> 300 ppm) values are omitted. The latter result, including its standard deviation, reasonably agrees with that for Pic du Midi 1881/82, which supports Müntz and Aubin's opinion that concentrations representative for uncontaminated air generally prevailed in the Plaine de Vincennes.

The majority of these data is centered around 280 ppm. The difference between the Pic du Midi series from 1881/82 and 1883 is obviously significant and considerably larger than what could be expected for samples taken in the same season of different years; most likely it does not represent a real atmospheric change, but must be due to some systematic experimental error. Since three of the four series at these two stations yield similar values, one may speculate that the results of the fourth, from Pic du Midi, 1883, may be too low, perhaps due to effect of sample storage.

There are two minor corrections to be applied to the data in order to obtain an estimate of the annual mean concentration. First, for calculating the CO_2 concentration in dry air one has to subtract the partial pressure of water vapour from the barometric reading. This is not mentioned in the – otherwise quite detailed – paper of Müntz and Aubin, so that it seems as if they did not take this effect into account. If applied this gives an upward correction of ca. 3 to 8 ppm for Plaine de Vincennes (temperatures ca. 10° to 25 °C; 100% relative humidity can be assumed in the water-containing aspirator volume) and of 2 to 6 ppm for Pic du Midi (0° to 15 °C). Second, the data are all from the summer half year, when CO_2 content is a few ppm below the annual mean value. Application of these corrections leads to estimated mean values near 285 to 290 ppm in the early 1880s, which appears to me a more reliable value than the 260 to 270 ppm suggested by Wigley, if Müntz and Aubin's data are accepted as a basis.

However, the absolute accuracy of these data is difficult to assess. Müntz and Aubin report only one calibration experiment, that yielded 297.5 instead of 302.0 ppm. Storage tests relevant to the problem of chemical attack of the glass were obviously not carried out. Furthermore, the difference between the Pic du Midi series indicates problems which were not completely mastered by even these skilled and careful experimenters. Therefore, an evaluation of their data is necessarily based partly on somewhat subjective judgment.

There is one more remark to the paper of Wigley (1983). Standard deviations indicated in his Figure 1 are incorrect, generally too small, e.g. those of the Pic du Midi and the Plaine de Vincennes series (see above), but also for the Baie Orange data (correctly 11.3 ppm instead of ca. 6 ppm).

The pre-industrial concentration and its variability play an important role in the carbon dioxide issue, and the reliability of early direct measurements is therefore by no means a purely academic question. For this reason a remark on the evaluation of data from Montsouris observatory by Stanhill (1982) is added, supporting the warning com-

ment by Waterman (1983). As pointed out by Waterman, the variations of the mean annual values given in Figure 2 of Stanhill (1982) cannot seriously be considered as representative for the free atmosphere. As mentioned by Waterman the monthly data given in Table I of Stanhill (1982) exhibit a sudden increase by about 30 ppm that can be precisely dated to have occurred between June and July 1890. Stanhill (1983) himself indicates the clue to this shift: the analytical method was changed in July 1890. The statement that the two methods were checked against each other and found to furnish the same results must be regarded with suspicion in view of the obvious discontinuity of the results. Although the formula of Leibniz *natura not facit saltus* cannot be maintained today, a quantum jump of the atmospheric CO_2 concentration is still vastly less probable than an experimental error of a scientist!

My impression from the study of these and other series of early CO_2 data is that it is very difficult, perhaps even impossible, to obtain reliable absolute values of the atmospheric CO_2 concentration from direct measurements in the pre-Mauna Loa period.

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