Anonymous Review of MS No.: acp-2009-120
"Sources and transport of delta 14C on CO2 within the Mexico City Basin and vicinity" S. A. Vay et al.
Special Issue: MILAGRO/INTEX-B 2006

The manuscript describes radiocarbon measurements of CO_2 samples collected over Mexico City aboard the NASA DC-8 during the MILAGRO field campaign. Results are reported for a total of 20 samples collected over 4 flights. However, much of the data analysis centers on 8 samples collected on March 16. Although the results are an interesting addition to the MILAGRO study, the manuscript as it stands has some serious problems in the presentation and interpretation of the data. Due to the extremely small data set, the manuscript is more in line with a technical note instead of an in depth research study of "…… the processes regulating the distribution of atmospheric ^{14}C in the MCMA……"(Pg 7216, first par.). Some sections are severely lacking in detail to the point that the reader cannot adequately evaluate the results without accessing many of the manuscript's references and no effort is made to compare the results with other previously published studies.

Much of the manuscript is dedicated to explaining 3 anomalously high results (>112 o/oo) and some "hot" carbon sources are invoked to explain them. These include bomb carbon sequestered in old trees, possible releases from a nuclear power plant and incineration of hazardous waste in private cement kilns. The release of bomb carbon from the burning of old trees is a well known source of excess ^{14}C, however the authors dismiss this source without much explanation (Pg 7223, Ln 23). The other sources considered by the authors, the Laguna Verde nuclear power plant located in Veracruz and various cement kilns licensed to incinerate hazardous waste, are not likely to be large ongoing sources affecting the entire area. The 3 high samples were collected in very different areas of Mexico, from Monterrey to Mexico City and one relatively high sample (95 o/oo) was collected about 200 miles south of Mexico City (Fig 2). No supporting evidence is given to indicate that releases from the Laguna Verde NPP are responsible for these anomalously high results over such a widespread area. There is also no evidence given that hazardous waste in the Mexico City area would be expected to contain large amounts of radiocarbon. There is some suggestion that the high values could be attributed to the incineration of medical waste (Pg 7224; Ln 11, Ln 21). However, radioisotopes used in nuclear medicine are normally short lived isotopes such as ^{99}Tc or ^{123}I and would therefore not be expected to contain anomalously high 14C concentrations.

The samples used for $^{14}CO_2$ determinations were originally collected for hydrocarbon / halocarbon analysis and it is assumed that these analyses were completed prior to the ^{14}C analyses. There are no details given as to the sample size used in the $^{14}CO_2$ analysis except for the statement (pg 7217, Ln 5) "….determined from air remaining in a select subset of whole air canister samples……". There are also no details given as to the treatment of the canister samples during the hydrocarbon analysis and prior to the ^{14}C analysis. Isotopic fractionation can easily occur during sample processing unless careful isotopic procedures are used. This would result in higher values for the heavier isotope especially when using very small sample sizes. Carbon-13 determinations are normally made along with the ^{14}C in order to determine the extent of isotopic fractionation during sample handling and analysis. The 13C/12C ratios can then be used to correct for isotopic fractionation if it is not too severe. Since no mention is made of the $^{13}CO_2$ results, and considering the implication of very small sample sizes, it can

only be assumed that these corrections were not made. It is therefore far more likely that the high values reported in the manuscript have resulted from sampling or sample processing artifacts than from the existence of multiple point sources of radiocarbon in the Mexico City area.

Some specific concerns are listed below.

1. The introduction is very short and does nothing to lay the background for the present study. Historical results of atmospheric $^{14}CO_2$ measurements should be reviewed to place the current results in perspective. Some relevant studies not included in the current paper are:

Meijer et al., Radiocarbon 48, 355-372 (2006).
Dutta, et al., Geophys. Res. Lett. 29, (1987).
Kitagawa, et al., Radiocarbon, 46, 901-910 (2004)
Levin and Kromer, Radiocarbon, 46, 1261-1272 (2004).
Levin et al., Geophys. Res. Let. 30, (2003)

2. The "Methods" section lacks any detail and too often the reader is referred to previously published work for any explanation of the sampling and analysis procedures used.

3. The measurement uncertainties are reported as +/- 2 o/oo (Pg 7218; Ln 4). It is assumed that this refers to the uncertainty in the accelerator mass spectrometry measurements only as it has been determined that the most accurate procedures will result in combined analytical uncertainties of +/- 3 o/oo (Meijer et al., Radiocarbon 48, 355-372). This was obtained with a 5 L sample size, duplicates run for each sample, and a 2 point calibration. It can only be assumed that the combined uncertainties in the present work would be larger than +/- 3 o/oo considering the implication of small sample sizes and the lack of opportunity for duplicate analysis.

4. Considering the levels of uncertainty outlined above, results should not be reported to the nearest 0.1 o/oo. Anything smaller than a whole number is not significant.

5. Figure 2 has 3 copyright citations at the bottom of the Figure and a "GOOGLE" logo in the lower right corner. Its use as presented would most likely violate copyright issues. In addition, it is very difficult to read and will probably become impossible to read when reduced for inclusion in the final document.

6. It is of concern that out of the 4 flights reported in the manuscript only 2 are examined in any detail and these 2 are treated differently. Considering the very small sample set, all the data points should be used in each data analysis in order to obtain a complete comparison.

7. Figure 4: Considering the very small sample set, clustering the samples obtained on March 16 is not statistically relevant. In addition, “Cluster B” contains the highest and lowest samples (taken in succession) so the average value is not significantly different from the average value in “Cluster C”, yet the slopes in Figure 4 are much different. Clustering these measurements yields misleading and confusing results.

8. Figure 5 is difficult to follow. Only the 8 samples collected on March 16 are plotted with selected tracer compounds. It is stated that samples collected on March 9 correlate with the tracers ACN, HCN, and isoprene (Pg 7221, Ln 22) but these data are not shown in the Figure. Data for all 20 samples should be shown. If a correlation is observed with any of the tracers, it should be displayed as an x-y plot giving the associated correlation coefficient instead displaying the data as a sample collection sequence.

9. Pg 7221, Ln 18: It is stated that as the CO_2, CH_4, and CO mixing ratios increase, the ^{14}C becomes more depleted. This is not evident from the data shown in Figure 6 since the sample with lowest CO_2/CH_4 and CO_2/CO and the sample with the highest CO_2/CH_4 and CO_2/CO have the same ^{14}C (69 o/oo). The ^{14}C values in the Figure are in the order 69, 66, 63, 59, 69-53. It cannot be concluded from this trend that the samples become more depleted, especially if error bars of +/- 3 o/oo are used. In addition, only the 6 samples collected on March 9 are used in Figure 6. What would the trend be if all samples were used?