

Interactive comment on “Comparison of measurements of peroxyacyl nitrates and primary carbonaceous aerosol concentrations in Mexico City determined in 1997 and 2003” by N. A. Marley et al.

Anonymous Referee #2

Received and published: 14 March 2007

Overall Comments This paper presents comparisons of measurements from field campaigns in Mexico City in 1997 and 2003 of concentrations of PAN (& PAN type compounds) and black carbon. These comparisons show a change in the character of the Mexico City air shed. This paper is well-written and should be published in ACP after addressing the following issues:

General Comments: The measurements show that PAN levels have decreased from 1997 to 2003 in Mexico City and the authors attribute this to reduced VOC and NO_x levels. This does appear to be the case, but there are a couple of other potential factors

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

that could be contributing to this observed decrease in PAN levels, and these should be discussed in greater detail.

The formation of PAN (and PAN type compounds) requires the simultaneous presence of NO₂ and peroxy radicals. Figures 5 and 6 hint at something in that the PAN concentrations in 1997 show maxima at or after noon, while in 2003, the PAN maxima are before noon. (By the way, this referee thinks that Figures 5 and 6 would actually work best if they were stacked one underneath the other with the same time scale shown in each so that the timing of these events could be compared directly in the figure.) Is it possible that the timing of the formation of high levels of NO₂ compared to the formation of high levels of peroxy radicals is mismatched in 2003 such that high levels of PAN are not seen as they were in 1997? For example, could the “rush hour” in Mexico City have shifted from 1997 to 2003 to earlier in the day, and as such, the maximum in the NO₂ concentration would occur before significant peroxy radical concentrations are built up? Boundary layer dynamics are obviously involved in this as well. Could some proxy for peroxy radical concentrations be plotted along with the measurements in Figures 5 and 6? How about modeled values of peroxy radicals? Overall, further discussion of the timing of the chemistry occurring in Mexico City is needed.

What about the temperature? PAN type compounds are greatly affected by small changes in temperature; for example, temperature swings of 15°C can occur between early morning and mid-afternoon in Mexico City, which changes the lifetime of PAN by an order of magnitude. (Example calculation: Morning temperature $\sim T = 15\text{ C}$, $k(\text{PAN decomp}) = 7.5\text{e-}5\text{ s}^{-1}$, lifetime of PAN $\sim 3.7\text{ hrs}$; Afternoon temperature $\sim T = 30\text{ C}$, $k(\text{PAN decomp}) = 8\text{e-}4\text{ s}^{-1}$, lifetime of PAN $\sim 0.34\text{ hrs}$) Were the measured ambient temperatures in 1997 and 2003 similar? Could heat island effects have changed the average ambient temperature in Mexico City? Could there be differences in local temperature effects at the two different sites from 1997 and 2003? This should be discussed and measurements of temperature should be included. (This is also mentioned by Anonymous Referee #1 with regards to the differences in time of year that the studies were

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

conducted, and this Referee agrees with that point.)

Specific Comments: Pg 1423, line 9: “1015” should be “10-15”

Pg 1424, line 5: It would be helpful to the unfamiliar reader to give some kind of reference value to give some perspective on just how high 300 ppb of O₃ is; for example the EPA or Mexican Government’s threshold for O₃ non-attainment could be included.

Pg 1428, line 22: It should be explained why NO₂ concentrations are estimated from NO_x-NO-PAN; it is obvious to this referee, but may not be obvious to everyone.

Pg 1429, line 7: A different technique was used to measure PAN in 2003 from 1997. The authors should comment at some point on how much this fact could potentially influence the comparison of these two sets of measurements. A short discussion of possible biases in either measurement technique would be helpful.

Pg 1430, line 16: The scale of Figure 1 makes it impossible to see the diurnal trend in PAN concentrations. It is suggested that the reader be pointed to Figure 5 to see this diurnal trend or that Figure 1 be expanded horizontally so that this can be seen.

Pg 1431, first paragraph: It is mentioned that traffic levels decrease during holidays in Mexico City; are there any numbers available to give a relative sense of the decrease in traffic during these times?

Pg 1431, line 9: The maximum O₃ concentration during the 2003 campaign reached higher than 135 ppb at the CENICA site (see Figure 6 in Dunlea et al., ACP, 6, 3163-3180, 2006). It is not clear which O₃ data the authors used for this study for the 2003 campaign; this should be specified in the experiment section and this reported maximum O₃ concentration should be corrected.

Pg 1431, line 22: The authors state that NO₂ levels have decreased from 1997 to 2003, but only cite the observed maximum values of NO₂ as evidence. Additionally, the example days in Figures 5 and 6 show maximum daily values for NO₂ of approximately 35 and 55 ppb for 1997, and approximately 140 and 70 ppb for 2003. Either different

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

example days should be chosen or average NO₂ concentrations should be reported to make this point better.

Pg 1432, line 11: “The PAN levels in Fig. 6 begin to drop as the black carbon concentrations reach their maximum supporting the suggestion of heterogeneous loss.” This may be the case on day 99 shown in Figure 6, but it sure looks like BC and PAN go down together (and rapidly) on day 98.

Pg 1433, line 1: Salcedo et al., ACP, 6, 925-946, 2006, show that BC is 11% of PM_{2.5}; this is consistent with the measurements presented here. It seems that this paper should be cited here.

Pg 1434, line 1: It is mentioned that hydrocarbon levels have decreased substantially in Mexico City since 1997, and one number (decrease of 39%) is provided. This referee thinks it would be useful to include more data to support this; in particular, it would be useful to list the decrease in levels VOC compounds that are precursors for PAN formation. Data could possibly be taken from Blake and Rowland, 1995, Velasco et al. (ACP, 7, 329-353, 2007) and Rogers et al. (Int. J. Mass Spectrom., 252, 26-37, 2006).

Pg 1434, line 7: “particularly black carbon” should be replaced with “including black carbon”. The average black carbon levels have decreased slightly from 1997 to 2003 (reported averages in this paper decreased from 15 to 10% of the measured PM_{2.5}) while the average fine aerosol concentrations increased slightly over that same time (average PM_{2.5} increased from 36 to 45 $\mu\text{g m}^{-3}$, which is an increase of 25%). Black carbon is undoubtedly still a problem in Mexico City, but it is not more of a problem than the overall fine aerosol levels, which represent a significant health threat in and of themselves apart from the black carbon content.

Figures: This is just the opinion of the referee, but it seems as though it would be much clearer if the figures were presented as four pairs of side-by-side figures instead of eight individual figures.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper