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Interactive comment on "The North Atlantic Marine Boundary Layer Experiment (NAMBLEX). Overview of the campaign held at Mace Head, Ireland, in summer 2002" *by* D. E. Heard et al.

Anonymous Referee #1

Received and published: 22 December 2005

Review of Heard et al., "NAMBLEX Overview etc.", ACPD 2005-0286

General comments: This overview of the NAMBLEX campaign will be quite useful to the participants and to dedicated readers looking for some background on the more specific papers in this special issue. The utility of this overview is somewhat compromised by its length, however, and efforts towards shortening the text and consolidating the figures are recommended before publication.

While this paper discusses measurements not specifically presented elsewhere, more could perhaps be done in this regard to quantify the performance of these critical measurements. While “detection limits” are presented in Table 1, no uncertainty estimates are provided for any of the measurements. For example, comparison of three ozone instruments suggest differences of 10% and 20% between them on average, with substantial point-to-point scatter and non-zero intercepts, but Table 1 gives only a “detection limit” of 0.6 ppbv. The ozone data is probably not known that well, given uncertainties of several ppbv in addition to large disagreements (for ozone) of 10 to 20% of the reported value. Adding a column to Table 1 showing measurement uncertainty, for all the reported measurements, is advised.

The description of the contamination of the NOx and NOy data seems to be incomplete. No attempt is made to quantify the acknowledged problem, which may make the data unusable in determining atmospherically-relevant levels of these compounds, due to acknowledged leakage from the PERCA inlet among other problems. The authors should at least provide guidance in how to justifiably interpret the NOx and NOy data in light of a real, but unquantifiable, possibly intermittent, and likely variable contamination. This particular UEA NOxy instrument has had a very long history of fundamental problems, and this appears to be yet another field deployment where the resulting data are substantially compromised. The use of the resulting NOxy data should be discussed in greater depth before any belief in their accuracy can be assumed.

Describing the observations carried out over two months as providing a “chemical climatology” or “meteorological climatology” is probably overly optimistic. While they do provide a very useful time series, and a statistically robust description of air masses during the campaign is presented, “climatology” might imply a longer time scale of relevance than the NAMBLEX experimental data can provide. I would suggest using a different phrase to convey what is intended by these statistical analyses of the observations.

This paper could be shortened considerably by trimming the introduction text. It is very well written, but is not required at anywhere near its present length in this specialized journal, where most of the readership has the necessary background to interpret the

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body of the findings without an in-depth introduction.

At 24 figures, some might be consolidated or removed to save space without much loss of content. Several of the draft figures are poorly legible due to their size in the printed version. Fig. 1,2, and 3 might be included into a single graphic, for example. Time series of wind direction, speed, temp, and RH could also be consolidated into one graph (using stacked axes) or eliminated altogether - T and RH show very little variability over the two-week period, esp. between different air mass periods, so could potentially be treated exclusively in the text. The data coverage graphic (fig. 5) is another ancillary plot that might be deleted in the interest of space. Fig. 17 did not seem to demonstrate much of interesting correlation between CN and tide, so perhaps showing a subset of the time series would be more illustrative. The trajectory data plots (figs 19, 20, 22, 24) are so small and appeared so similar that some care in picking out just the major details would be appreciated.

Finally, addressing and quantifying the data uncertainties, especially in ozone and nitrogen species, would seem to be required before this manuscript is acceptable for publication.

Specific comments.

Abstract. Using data from a months-long campaign to construct a “chemical climatology” is a bit overstated, I think, given the normally accepted use of the word. Most dictionaries define “climate” as a state determined over a period of years. Please rephrase here and throughout the manuscript, for both the intended “chemical climatology” and “meteorological climatology” descriptions.

3. Measurements of atmospheric composition

Page 12193, first paragraph: Speaking of ozone, “The agreement between the instruments is good.” This comment should be deleted. The following paragraph provides information that quantifies the agreement, so this qualitative comment is not needed.

Page 12193, second paragraph: please provide an rˆ2 value for these regression fits. The comparison data show substantial scatter, so quantifying the degree of correlation would be useful.

Page 12193, second paragraph: The three ozone measurements were performed using UV absorbance instruments, which intrinsically provide absolute data and cannot be calibrated. When these commercial instruments, provided with adjustments to their output, are “calibrated” to match another instrument, actual problems in the instrument are being masked by this procedure. “Calibration” in this manner deviates from the Beer-Lambert law and should be avoided. Instead of adjusting the output from an absorption instrument, the investigators should clean or replace the part of the instrument that is causing the deviation from nominal operation. This should be noted in the text, the degree of “calibration” specifically stated for each instrument that was adjusted to force an agreement with the NPL certified standard, and the resulting uncertainty in the ozone data (of at least 3-4 ppbv plus 10 to 20% of the measured value) stated here. This uncertainty should be taken into account in the ensuing analysis. Differences of 10-20% are very large and suggest substantial problems with one or more of the ozone instruments. How stable these instruments were over time is also a point that should be discussed.

Page 12193, second paragraph: What does “PS” signify in equations 3 - 6? Please define.

Page 12193, second paragraph: “The observed differences Ě are most likely due to losses upon the surfaces of inlet tubing. As all differences were within 20% of one another, these differences were not investigated further.” This is a surprising conclusion, as ozone measurements are routinely compared and, with well-operated instruments, are often within <1 ppbv and a few percent of each other. Ignoring a 20% error in ozone can adversely affect the interpretation of, e.g., HOx measurements. The contribution of HCHO photolysis to the radical budget is often around 10-15%, with ozone contributing approximately 75% of the total. Errors in the ozone determination can lead to very large errors in estimating the contribution of other oxidants to the radical budget. 20% losses of ozone on inlet tubing is surprising, given the relative ease of sampling ozone generally described in the literature. Was this supposed loss constant over time, or not? If it was assumed constant, by what mechanism was this occurring? Without further substantiation, this inlet loss explanation is suspect, and in any case calls the ozone measurements into further question. Please reconsider the sources of disagreement in these critical measurements, quantify the resulting ozone data uncertainty (and revise Table 1 accordingly) and provide some guidance for users of these data in light of the large problems in this measurement.

Page 12197, first paragraph: HCHO measurements are described as correlated in time but with an offset. An additional sentence quantifying how well they were correlated (providing an rˆ2 value) and giving the magnitude of the observed offset - and the median ambient HCHO value, to put the magnitude of the offset into perspective- would be very useful here.

Page 12199, first paragraph: The authors suggest that differences between the in-situ and long-path NO3 measurements provide “Ěa unique opportunity to examine horizontal gradients in the radical’s (sic) concentrationĚ” This implicitly assumes that the two measurements would agree perfectly when compared side-by-side, so the observed differences are real. Was this agreement demonstrated? The ozone measurements had 10-20% differences associated with them, and one wonders if the ozone measurement error might have been interpreted as a horizontal gradient had they not been co-located. What confidence is there in the NO3 measurements, that permits horizontal gradients to be inferred from these different instruments? Please elaborate, or reconsider this interpretation.

Page 12199, second paragraph: What kind of photolysis converter was used for NO2? How effective was this conversion? How stable was this conversion over time?

Page 12199, second paragraph: “Nitric acid was determined by subtracting the signal from two identical NOy convertersĚ” How identical? How was this verified? If the two “identical” converters performed as well as the ozone measurements, above, one would infer 10-20% of NOy was nitric acid, when in fact there was none. Please elaborate on how this HNO3 measurement was validated under the field conditions of the NAMBLEX campaign, and its associated uncertainty.

Page 12199, third paragraph: “The measurement(s) Ě were unfortunately compromised by local contaminationĚ” The possibility that the common inlet (shared with the PERCA, an instrument that uses very high levels of NO as a reagent) contaminated the NO, NO2, NOy, and HNO3 data is not ruled out. The assertion that “the measurements can be used for many purposes” is totally unproven, by any objective measure. Figure 12 does not even attempt to screen the hourly averages for the known contamination! Please explain how useful determinations of “pristinely clean, marine background air” can be made when an intermittent contamination problem of unknown origin is acknowledged. What guidance, by the authors of this overview document, can be given to users of the NOx and NOy data, in light of this problem? Are there any checks that can be applied to see if the data make physical sense? Can the spectral radiometer provide useful constraints, using the photo-stationary state analysis, on the measurements of NO and NO2? Certainly there will be substantial error in this analysis from the large uncertainties in the ozone measurement alone, but it should be evaluated nonetheless.

Page 12216, first paragraph: Plots of CO vs O3 show mixing lines, unless a strong case can be made that photochemical production is the largest contributor to the observed slope of the CO-O3 relationship. This must be proved in each instance, or the inference of ozone production is tenuous at best. Please provide some additional justification as to the legitimate interpretation of the data solely in terms of production, and not simply as two different air masses mixing.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12177, 2005.