

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.

D. E. Heard et al.

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The authors thank the referees for their thorough and critical reading of this manuscript, and their very helpful comments.

General comments to both referees

Both referees comment on the length of the paper. We feel that the length of the paper is justified as it is a support paper to the others in the NAMBLEX special issue. The subsequent papers are all much shorter in length as a result and therefore rely heavily on the overview paper for information about the site and data coverage. However, we agree that the number of figures is rather excessive and so have addressed the

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suggestion of merging and removing some of the figures and this issue is dealt with in more detail within the individual specific comments below.

Referee 1 General comments

(1) An additional column has been included in Table 1 for measurement uncertainty of the reported measurements.

(2) At the submission stage to the database, a flag was added to identify sudden spikes in the NO record from the NO_x instrument (which were only seen early on in the campaign), and which may have resulted from local contamination (but see below), and all of these points were removed prior to any presentation of data or analysis. The origin of the spikes is unknown (e.g. electronic or contamination), and they were classified using local wind-direction, wind speed and CPC counts. Some were not correlated at all with particle count from the CPC, suggesting it is not a site-wide meteorological feature, and these were of very short duration (< 3 data points) and large, and hence extremely easy to identify and remove. Others, which were not as intense and longer in duration (but still less than a minute or so), were correlated with CPC count, suggesting a site-wide meteorological event. However, they were quite obvious and as they were not representative of the general NO levels over that period, they were not used for modelling or for calculating average values for that period. Following the removal of flagged data, the remaining NO_x data should be of high quality and can be used without undue concern. There were sometimes very low levels of NO observed at night by the NO_x instrument (5 pptv), and to investigate this NO levels were also measured at various heights from the ground: 6 cm (right at the soil/bog surface), 1m, 5m, 7m and 20m. The data suggest that there is a source of data from the peaty soil itself. In other papers in this issue (Bitter et al. 2005b, Saiz-Lopez et al. 2005b) it is speculated that emissions from the land at night may explain why concentrations of NO₃ measured by Cambridge using the in situ BB-CRDS method, located at the shore site, were much smaller than the NO₃ concentrations measured by the long-path DOAS instrument which samples largely over the ocean. Modelling has shown that the fast

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reaction between $\text{NO} + \text{NO}_3$, using the measured NO on land at night, can explain the difference in the NO_3 levels, giving support to the quality of the NO measurements (Bitter et al.). In this overview paper the authors have been honest about spikes in the NO_x record being due to possible local NO contamination during the early part of the campaign. The spikes had in fact already been removed from Figure 12 (now Fig. 10), and these data were not used in any subsequent analysis or as input to models. Length precluded a detailed description of the possible contamination, but it is hoped that the above provides a more complete account, and shows that steps were taken to quantify the problem.

There is one statement though in the paper that is not correct, and the authors would like to apologise for the error. The paper states that the NO_x and the PERCA instruments shared an inlet. This is not true, and cannot be, as the PERCA instrument adds large levels of NO and CO to convert HO_2 and RO_2 radicals into NO_2 which is then detected via luminol. Upon examination of photographs taken at the site during NAMBLEX it is clear that the PERCA and NO_x inlets are separated by several metres. Both inlets draw air into their instruments at significant flow rates and so there cannot have been any leakage from the PERCA inlet (and there is no evidence for this). We apologise if the wording in the paper was misleading in this regard. These statements have now been removed.

A second NO instrument from the Leeds group (TECO 42C), with a 50 pptv detection limit, was also deployed during NAMBLEX at the FAGE container, located approximately 25m from the NO_x instrument inlet. Although this instrument did not have the required sensitivity to measure in the predominantly clean air experienced during the campaign, and hence the data coverage is very sparse indeed, it did help to confirm that spikes in the NO_x record, observed only early in the campaign (and which were removed prior to any data analysis), and which may have been associated with a local contamination, were not indicative of the site as a whole. For very limited periods when sufficiently polluted air reached the site (rare during NAMBLEX), the Leeds instrument

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could also confirm the levels of NO observed by NOxy instrument.

(3) The implication that the phrases “chemical climatology” and “meteorological climatology” were applicable to much longer timescales than are described here has been addressed in the revised manuscript and the phrases, including those used in the sub-headings, have been extended to include “for the duration of the campaign”.

(4) We have looked through the introductory text and have shortened where we feel the material is not crucially important to the overview paper. The list of AGAGE sites has been removed. However, one comment is pertinent here. NAMBLEX was the 3rd intensive campaign funded by NERC involving the UK atmospheric field measurement community at Mace Head. Earlier campaigns had their successes, but there were deficiencies in the coverage and quality of the measurements, due to techniques not having been developed, or instruments being in their infancy. The NAMBLEX campaign also involved extensive involvement by atmospheric physicists who made measurements of the structure of the boundary layer which helped to interpret local versus synoptic flow, and aided the classification of air masses. Such involvement is not always the case and so the introduction has a short section outlining the role played by the dynamics measurements. In addition the split deployment of previous campaigns at the top and bottom site caused difficulties in the interpretation of data. Hence it was important to discuss NAMBLEX in the context of previous work at Mace Head in some detail, and also to compare with other field campaigns performed elsewhere in the marine boundary layer. None of the other papers have an introductory section putting the campaign in context with others in the MBL, Mace Head or elsewhere, but rely on the overview paper instead, and hence although making this paper slightly longer, results in a major saving of space overall.

(5) We have removed or merged some figures at the request of the referee, as described below.

The authors feel that Figs. 1 and 2 should be left as individual figures. The additional

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papers in the special issue refer specifically to the detail shown and we feel that one collated figure would be cluttered with too much information.

The campaign meteorology has been discussed in considerable detail by Norton et al., 2005 (this issue) and so Figures 3 and 4 have been removed and treated exclusively in the text.

Figure 5 (now Figure 3), which details the data coverage of various species during NAMBLEX, is an important Figure, as it shows the overlapping periods of key species, and is very useful for cross-referencing purposes when individual species included in various models are discussed, and the authors hence would like to keep this Figure, and it remains in the revised manuscript.

Figure 17 has been removed as suggested by the referee.

The trajectory plots given in Figures 19, 20, 22 and 24 (now Figures 16,17,19 and 21) have been made much clearer in the revised version as suggested by the referee.

(6) Data uncertainties are now given in Table 1.

Referee 1. Response to specific comments

(1) Abstract: As stated above “chemical climatology” has been replaced with “chemical climatology for the duration of the campaign”, and “meteorological climatology” with “meteorological climatology for the duration of the campaign”.

(2) P. 12193 The comment “The agreement between the instruments is good” has been deleted.

(3) P. 12193 R2 values have been provided to quantify the degree of correlation between the ozone instruments.

(4) P. 12193 The authors agree that the “calibration” performed by adjusting instrument output in fact masks problems with the ozone instruments. The “drift” in measurements is thought to be a result of a drift in the temperature and/or pressure readings within

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the instrument itself, which then give an incorrect absorbance reading. A line has been added to the text to highlight this issue. As requested the relative uncertainties have been included into Table 1 and these include the uncertainty with respect to the DEFRA instrument, the uncertainty with respect to the Primary Standard (PS) and the stability error. This is discussed in an additional footnote to Table 1.

(5) P. 12193 PS-Primary Standard has been defined in equations 3-6.

(6) P. 12193. Ozone measurements. As O₃ is such a important tropospheric species three independent measurements were made during NAMBLEX and these are shown in Figure 6. Despite the additional uncertainties resulting from multiple instruments measuring the same trace gas the authors feel that having three ozone instruments deployed during NAMBLEX does represent an advantage. It has been noted elsewhere that ozone concentrations can vary around a field site, perhaps as a result of different sampling heights or microenvironments (lee of building etc.), and it was desired to quantify any variation as much as possible. Details of the three instruments are: (1) DEFRA (the permanent instrument at Mace Head) used a Monitor Labs UV spectrometer absorbing at 254 nm to make measurements at a height of 3 m up the 23 m tower (3m from the ground) every 10 s, reporting them as 1 min averages for the entire campaign. (2) The University of Leeds used a TECO 42C at a height of 5 m (from the ground). (Fig. 1) and reported 1 minute averages for the entire campaign, (3) The University of Leicester also used a TECO 42C from building B at a height of 4 m (from the ground). In fact Figure 7 (Figure 5 in revised manuscript) showed the data for the entire campaign not just for the periods 17 – 20 August and 26 August – 4 September and the caption and manuscript have been altered accordingly. In addition to the best-fit-linear regressions for the entire campaign, in the revised manuscript these have also been provided for the periods 17–20 August and 26 August – 4 September when all three instruments were measuring together.

During NAMBLEX all three instruments were independently calibrated on site by the National Physics Laboratory (NPL) using a certified standard. This process corrects

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the absorbance reading for the temperature and pressure measurement drifts within the respective instruments. All three instruments were very close to this calibration standard. In addition a GAW O3 audit was carried out by EMPA Swiss Federal Laboratories for Materials Testing and Research during the campaign (21–26 August) and all three instruments were checked against a TEI-49C PS (Primary Standard). Laboratory tests have shown the stability of the ozone instruments to be <2

The Leeds ozone measurements were used to constrain the models for the calculation of free-radical concentrations (Sommariva et al., 2005a and b) as the instrument inlet was positioned closest to where the HOx measurements were made (within a few metres). Errors resulting from ozone measurement uncertainty were taken into account in the final modelled data. The DEFRA data series, which was considerably noisier than those of the other instruments, was used for the interpretation of sampled air masses and correlations with longer lived species. The Leicester instrument was used on the aircraft for a significant part of the campaign and so was and was not on site at Mace Head at these times.

We agree that the inlet loss explanation for the difference in ozone values is rather speculative, and we have no clear evidence to support this, hence this comment has been removed and replaced with “the reason for the discrepancy remains unknown”. Differences in ozone concentrations have been noted at other campaigns, even when instruments are extremely close to the correct value when calibrated by an NPL standard before and after the campaign, and further experiments to test the hypothesis of differing inlet losses are being carried out.

(7) P.12197 An R2 value has been provided to show the correlation between the HCHO instruments and the magnitude of the offset has been added. However, reference is made to Still et al., 2005 where these issues are described in extended detail.

(8) P. 12199 The differences in NO3 concentrations measured in situ by the BB-CRDS instrument and the long-path DOAS are presented in detail by Bitter et al, 2005b, to-

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gether with a discussion of the evidence for horizontal gradients in NO₃ concentrations and their interpretation. A model is presented to support the interpretation. It is not possible to run the BB-CRDS and DOAS side by side as one has a footprint of 2m, whereas the other has a path length of 2 x 4.2 km. The papers that describe these instruments also give details of the uncertainties in the instruments, and detection limits, which allow the statements on the gradients to be made with confidence. It is not sensible to elaborate in detail on this in the overview paper, for reasons of space, and reference is therefore made to these papers for the interested reader.

(9) P. 12199 The paragraph describing the NO_x instrumentation has been expanded in-light of the comments made by the referee. A description of the NO₂ photolysis converter has been included detailing the conversion efficiency and its stability with a reference for a full description. Uncertainties in the measurements have been included within Table 1. It is agreed that a reliable HNO₃ measurement requires that the equivalence of the NO_y convertors can be proven. In addition the measurement of NO_y and subsequent calculation of nitric acid has been described including information about the calibration techniques and conversion efficiencies.

(10) P.12199 The comment on the shared inlet was discussed above. The NO_x and PERCA inlets were not shared, and this statement has been removed. Again, we apologise for this misleading statement, which will have prompted the subsequent concerns of the referee, but which are unfounded. The contamination spikes which proved problematic only at the beginning of the campaign have already been removed from the hourly averaged data shown in Figure 12 (now Figure 10 in the revised MS), and thus it is incorrect that no attempt had been made to screen the hourly averages. All data were carefully screened and flagged prior to any data submission, and the easily identified contamination spikes (from whatever source) have all been removed prior to any averaging or further use of the data. For the reasons already given above in response to general comment (2), we feel the data can be used with confidence for other purposes, e.g. as inputs for constrained models.

(11) P.12216 During NAMBLEX predominantly clean air of marine origin was sampled, which allowed the major objectives of the project to be achieved. The periods when polluted easterly air was sampled, where NO_x levels were higher, were short. Hence despite previous observations of summertime regional scale photochemical ozone production at Mace Head in European air masses (Derwent et al, 1994), there is not enough evidence from NAMBLEX to argue whether the same is true in the polluted periods. A Lagrangian chemical model is needed to investigate this further, which is beyond the scope of this overview paper. Although Figure 23 (now Figure 20) does show positive CO-O₃ relationships, the referee is correct in suggesting that these may be due to mixing and not solely ozone production. This section has therefore been restructured and references to Figure 23 (now Figure 20) have been altered to account for this suggestion.

Referee 2. The only general comment was on length which was addressed above.

Response to specific comments.

(1) P12180 L5 RO₂ has been changed to HO₂ + RO₂

(2) P12186 L11 The title of section 2 has been changed to “Description of site, measurements and model activities”.

(3) P12193 L1 The heights above ground of the sampling inlets for the individual ozone measurements have been included in brackets after the introduction of the instruments.

(4) P12193 L12 The reference to previous ozone measurements at Mace Head has been amended from Derwent et al, 1994 to Simmonds et al, 2004 and in-light of this publication, the sentence now reads “ Ęwith a campaign average of 29.0 ± 6.5 ppbv, within error of previous average summer ozone measurements at Mace Head between 1988 and 2002.”

(5) P12193 L13 The statement “The agreement between the instruments is good” has been removed. The measurement uncertainties on the ozone measurements have

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been further clarified in Table 1 and indeed the most relevant spatially applicable data have been used for the modelling (the OH/HO₂ and Leeds O₃ were measured at the same point).

(6) P121934 L23 The units of ppbV for CO and C₂H₂ have been included in Equation 7.

(7) P12195 L10 The reference of Novelli et al 1999., for H₂ detailed in paragraph also applies to the comment from the referee about soil uptake. A further reference for H₂ measurements and uptake by soils has been included to add weight to these measurements.

(8) P12195 Eq. 8 and 9 The units of ppbV for CO, CH₄ and for C₃H₈ have been included in the equations.

(9) P12197, L4 The magnitude of the offset between the HCHO measurements has been included in the revised MS, but this is discussed in detail by Still et al., 2005.

(10) P12197 Although two measurements of peroxides were made during NAMBLEX by UEA and the University of Leeds, the data analysis and comparative work is far from being complete. Hence we are unable to comment on the agreement between the two instruments at this stage. Reference is made instead to the future publication Jackson et al. (2005) which will form part of this special issue.

(11) P12198, L3 CHCl₃ was also measured by both the Universities of Bristol and York. The sentence has been rephrased to clarify this.

(12) P12199 L22 The paragraph describing NO_x measurements now includes information on the NO_y converter and the uncertainties on the NO_y and HNO₃ measurements have been included in Table 1. Direct measurements of the nylon tube efficiency were not done although thought to be more than 95

(13) P12203 L12 The reference for FAGE of Hard et al has been added.

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(14) P12234 Fig 4 AC and C have been defined as Anticyclonic and Cyclonic respectively in the new Figure 4.

(15) P12237 Fig 7 (now Fig 5) Units of ppbV for ozone and 1:1 agreement line have been added to Figure 7 (now Figure 5) as suggested.

(16) P12239 Fig 9 (now Fig 7) The H₂ concentrations are discussed by Smith et al. and Sommariva et al. in this issue for the budgets of HO_x, and although there is not a significant trend, as noted by the referee, it is a valuable data set nonetheless, as H₂ is rarely measured during intensive field campaigns. So we have decided to retain the H₂ figure, although as discussed above, several other figures have been removed to reduce the length.

(17) P12241 Fig 11 (now Fig 9) The units of pptV have been added to the ethane, propene and isoprene time-series in Figure 11 (now Figure 9).

(18) P12243 Fig 13 (now Fig 11) The legend details that NO, NO₂, HNO₃, PAN, and organic nitrate are included in the calculated NO_y.

(19) P12246 Fig 16 (now Fig 14) The colours on Figure 16b (now Figure 14b) have been adjusted for clarity.

(20) P12247 Fig 17 The plot of CN and tidal height showed little interesting correlation so has been deleted from the publication.

(21) P12249-12250 Figures 19 and 20 (now Figures 16 and 17), have been made much clearer in the revised version.

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