

***Interactive comment on “Ambient formaldehyde measurements made at a remote marine boundary layer site during the NAMBLEX campaign – a comparison of data from chromatographic and modified Hantzsch techniques” by T. J. Still et al.***

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We would agree with the referee in that the current situation with a discrepancy between the two datasets is less than ideal, nevertheless, we believe that due to the importance of formaldehyde as an atmospheric intermediate and previous discrepancies in intercomparison experiments, it is important to present both datasets in the open literature along with a discussion of possible explanations. The level of agreement on trends of formaldehyde concentrations, e.g. inset to Fig 3, gives us confidence that we are both sampling the same general air mass and making measurements at low concentrations with high precision. In addition to the absolute concentration data, both

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techniques clearly agree on the observation of a significant diurnal variation during stable weather conditions, something that has not always been observed in previous studies in the marine environment.

Specific points 1) Formaldehyde:acetaldehyde ratios - It is certainly possible that sampling undertaken by Lewis et al. is subject to similar uncertainties, however, Tanner et al measured formaldehyde and acetaldehyde using the same technique (DNPH cartridges) and hence the ratio should be less susceptible to systematic errors. We therefore believe that the Tanner ratio should be compared with the measured ratios from NAMBLEX. Within error (n.b. regression equation with errors has been added in section 4.2), the gradients of the regressions of formaldehyde to acetaldehyde are the same for the Tanner work and the UoL/Lewis et al. measurements, but not with the UEA/Lewis et al. measurements. It is of course possible that the error lies with the measurements of Lewis et al. 2) Sampling lines - The effects of the length of the sampling lines were investigated both during the campaign and during the subsequent laboratory intercomparison at NPL. No effects were observed. Material has been added to section 3.1. Sections 3.1 and 5 also contain some material on possible interferences from water vapour. 3) Altitude of sampling - Given the relatively low deposition velocity and at times exceptionally good correlation in concentration variations, we don't believe that differences in altitude are likely to be important. 4) Coil length - The stripping coil length is approx half the length used by Lazrus et al (Anal Chem, 60, 1074,1988) though in the original lab tests (Cardenas PhD thesis, University of East Anglia 1997) , lengthening the coil gave no improvement in signal indicating that equilibrium had been reached in the system. At atmospheric pressure, particularly in turbulent flow, the rate of uptake of HCHO is essentially limited by the rate of conversion of the HCHO(aq) to the diol (Jayne et al. J. Phys Chem 96, 5452, 1992.) which has a rate constant of  $>=103$  at 298 K and results in greater than 90% uptake in 2 ms. 5) Coil temperature - There will be some effect of temperature on the overall uptake rate which is made up of many competing temperature dependent processes. The rate of reaction of HCHO will increase with temperature and the uptake coefficient is inversely related to temperature

(Jayne et al 1992). Given the Henry's law constant for HCHO (at a pH of 1) of  $2.97 \times 10^3$  at 298 K, our sample flow rate of 1.5 slm and stripping coil flow of 0.4 ml/min, we would expect a theoretical maximum stripping efficiency of 92.5%. A temperature reduction of 20 K has been shown to give approximately a four fold increase in the Henry's law constant (Dong and Dasgupta Environ Sci Technol., 20 637, 1986) this results in a limit of 97.8% efficiency at 278 K. Our use of a gas phase calibration allows us to account for a less than 100% stripping efficiency at constant temperature, but variations between the sampling and calibration temperatures will cause slight errors, although in previous laboratory and field experiments we have never observed any significant relationship between temperature and our calibration response. The temperature of the laboratory in which the instrument was housed varied by  $\sim 5$  K, introducing a slight error in the measured concentrations and the effects of this have been included in an updated section on precision at the end of section 2.3. 6) Boundary layer height - Value taken from typical NAMBLEX measurement (reference inserted in text). Variations of the MBL height should be relatively small. 7) Figure 8a does show two days of modelling data. The MCM model is updated by inputting the measured concentrations of long lived species but as a box model we appreciate that it is not the perfect tool to investigate diurnal variations of a relatively long lived species such as formaldehyde. In some cases the model gives good agreement with the short time structure e.g. the rapid rise at 12.00 on JD228 (fig 8b), but in general we would not expect it to produce all the short time variations in concentrations of such a relatively long lived species as formaldehyde. In figure 8a, the MCM clearly does not reproduce the diurnal variations observed by both techniques. However, the aim of the modelling was to compare the average values and not the short term variations. 8) Table 1 - Only a relatively few data points were collected by the TDLAS technique in the Cardenas paper and these have significant scatter. The measurements are mentioned in the text, but given the scatter, we don't feel it appropriate to include the data in a table. 9) The Hak et al. reference is included in sections 1 and 5.

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