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Interactive comment on "Halogens and the chemistry of the free troposphere" *by* D. J. Lary

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D. J Lary presents an interesting study of importance of halogens in the free troposphere, using data assimilation analysis of sulphate aerosol, ozone, HCl, HNO3 and water vapour. His results show that Cl can significantly contribute to methane oxidation, to NO to NO2 and OH to HO2 ratios and that heterogeneous hydrolysis of ClONO2 and BrONO2 can be important for HNO3 production in free troposphere. Halogens has been so far mostly considered in stratosphere and in the marine boundary layer as stated in the paper. The study of D.J. Lary presents new results on role of halogen chemistry in free troposphere, however there exists studies that might be worth mentioning: a box model study of Hendricks et al. (1999) that estimates the effect of halogen chemistry in the tropopause region and a recent study von Glasow et al. (2004) that have studied effects of bromine chemistry in troposphere with global CTM, htese are not mentioned in the paper. The fact that the study is brief would not be of disadvantage by itself if the paper had presented enough information about how the results presented in figures 1-4 were obtained. This was, however, not done. What

time period was simulated? Part of the shows the role of BrONO2 hydrolysis in HNO3 formation, but how was the bromine calculated in the model? How was the heterogeneous reactions treated: what reaction probabilities or sticking coefficients were used for ClONO2 and BrONO2 hydrolysis? Why was just the time point of mid October chosen? From Fig. 1 it can be understood that it is a snapshot at 11:15, how would part e and f of the figure look like if an average over a longer period would be chosen? I would like if those questions would be answered in the paper. I have few technical comments to the paper: p. 5370, l. 7-8: OH reacts with CH4 and CO within a second - at 293K, 1013hPa and 1.72 ppm CH4 (ground) the lifetime of OH in CH4+OH is 4s, at 252K, 360 hPa and at the same mixing ratio of CH4 (upper troposphere) the lifetime is 25s. For the CO+OH reaction the corresponding lifetimes are 2 and 18s. Statement within seconds would be more appropriate. p. 5370 l. 14: Rate of reaction in Eq. 4 is extremely slow, methane oxidation in troposphere is not usually initiated by this reaction. p.5371, l. 2-3: Halogen catalyzed methane oxidation can play a significant role in Ě explain how or add a reference p.5372, l. 2: DeMore et al. (2000) gives compilation of rate constants, is not showing that key channels in HNO3 production are reactions X and Y. p. 5372, l. 5: DeMore et al. (2000) is not the best reference strenghtening that BrONO2 and ClONO2 hydrolysis are routinely considered in stratosphere (as a compilation it rather lists all reactions that were investigated) P. 5377, Fig. 1: The figure is too small. The text on axes is not possible to read and colours in the rings are impossible to distinguished even if maximum enlargement is used.

References: Hendricks, J., Lippert, E., Petry, H., Ebel, A., 1999. Heterogeneous reactions on and in sulfate aerosols: Implications for the chemistry of the midlatitude tropopause region, J. Geophys. Res., 104, p. 5531. Glasow, R. , Kuhlmann, R. , Lawrence, M. , Platt, U., Crutzen, P., 2004. Impact of reactive bromine chemistry in the troposphere. Atmos. Chem. Phys. Discussions l, p. 4877-4913.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5367, 2004.