Interactive comment on “A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 1 – bromide solutions” by B. M. Matthew and C. Anastasio

Anonymous Referee #2

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General comments

The manuscript presents a new and attractive method for the determination of steady-state concentrations and rate of formation of reactive halogen species in aqueous solution, which can be applied for environmental analysis such as seawater, sea-salt particles and possibly snowpack samples. The method presents an alternative approach to flash photolysis and pulse radiolysis techniques to study reactive halogen species in solution, however the sample preparation required for the determination of 3-bromo-
1,2-propandiol (3BPD) is not a simple procedure. This requires several steps and is a time consuming process (the analysis time alone is more than 1 hour as shown in Matthew and Anastasio, 2000)

Whereas the kinetics and the data treatment have been thoroughly described, the analytical methods used in this study should be presented in a more complete way. In particular, details on the determination of the allyl alcohol losses are needed. The manuscript should give an indication of the uncertainties on the measurements reporting the errors for the calibration curve and the detection limit. Please give a reference if it has been published somewhere else.

The authors stated that the method should work for environmental samples and more details should be expected in Part 2. However, the application of the method is restricted to laboratory conditions so far and the success of the method with real samples remains only hypothetical. This is also the case for Part 2.

A detection limit for 3BPD of 0.17 $\mu$g l$^{-1}$, which was reported for spiked water (Matthew and Anastasio, 2000), can be a limitation in the application of the method to real environmental samples, especially at low concentration of allyl alcohol where the calculated rate of formation of 3BPD are below 1 nM min$^{-1}$. How strong is the influence of high concentration of halides on the detection limit for the analysis of 3BPD?

**Recommendation:** We can only suggest publication after major revision according to the points addressed in this review

**Specific:**

**Page 910, line 22:** The Authors stated that the polymerization rate constants considered in their study are suitable for most of the cases but not at higher allyl alcohol concentrations where a stronger effect of the polymerization processes should be expected. Isn’t it a clear indication that polymerization reactions are overestimated in the current model? How does this consideration influence the data treatment? As shown
Page 934, Figure 3: In the experiment conducted in absence of bromide, the plateau observed in the rate of loss of allyl alcohol might be probably attributed to the total consumption of OH radicals produced from the photolysis of $[\text{H}_2\text{O}_2]$ (exclusive source in the system under the stated experimental conditions). An OH rate of formation of about $0.48 \mu\text{M min}^{-1}$ can be derived considering the rate of photolysis of $j = 4 \times 10^{-6} \text{ s}^{-1}$ and the initial concentration of $[\text{H}_2\text{O}_2] = 1\text{mM}$ as presented in the paper. It is not clear why the model is overestimating the rate of loss of allyl alcohol.

Pages 936-40, Fig. 4-6: How are the experimental rates of loss and the rates of formation derived in the Figures? Is any data treatment performed? For a set of experiments, it will be helpful to have also the plots of the loss of allyl alcohol and formation of 3BPD at each allyl alcohol concentration as supplementary material.

Supplementary material:

a) In the presented set of reactions “Br- Full Model” there is no reaction between OH radicals and the newly formed 3BPD. Has this been evaluated in separated experiments? Can a fraction of 3BPD be further oxidized by OH at longer reaction time?

b) In the kinetic model no reactions have been included that lead to the formation of poly-brominated species. Is there any evidence of formation of poly-brominated species at longer reaction times? Would this influence the data treatment?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 899, 2006.