

## ***Interactive comment on “Different photolysis kinetics at the surface of frozen freshwater vs. frozen salt solutions” by T. F. Kahan et al.***

**Anonymous Referee #2**

Received and published: 3 June 2010

The paper provides new and important information regarding photochemistry of harmine in aqueous solution and at the surface of ice and frozen salt solutions. The paper shows two major points: (1) the photolysis of this aromatic compound is much faster in doped ice than in aqueous solutions, further indicating that the QLL environment, where it is likely to be present, behaves differently than liquid water. (2) In frozen salt-solutions, at temperatures above eutectic point, the chromophore is present in liquid brines, showing similar photodegradation rates as in aqueous solutions.

These conclusions are important with regard to understanding photochemical process in ice/snow and to our ability to apply laboratory data to ambient conditions. The paper well written and fits publication in the ACP journal.

Specific Comment 12065 line 10 – The authors cite previous studies that showed that  
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the observed photolysis rates in bulk ice and aqueous solutions are similar. The term “bulk ice” in this context is not very clear and can be confusing, as we know that most organic solutes are not present in the ice matrix itself but in the boundaries between grains and on their surfaces. Furthermore, assuming that some of these “bulk ice” studies were done with thicker polycrystalline ice, what does that imply on the quantum yields in these two environments? If the light flux reaching the chromophore embedded in ice is much lower (due to scattering) than in aqueous solution, the yields are actually higher in the frozen environment. Can the author refer to this point?

In any case, a comment should be added that even if photochemistry in aqueous solutions represent the process in frozen salts, one needs to remember that under ambient conditions, where ice is not a thin clear layer, actual rate may differ from those in solution due to different light flux in the ice/snow layer.

In the experimental section it says that the ice samples were prepared by freezing a solution in the chamber with cooled base (page 12067 line 4). Does that mean that freezing was progressing relatively slowly from bottom to top? What was the freezing rate? Since the solutes are expected to accumulate in the last areas to freeze (top surface of the ice sample in this case?), it is important to mention this information in the text as well as provide more description of the generated ice; for example: was it clear, opaque, were trapped bubbles presence? etc.

Since the ice samples might be very heterogeneous and solutes are excluded from ice matrix during freezing, I am not sure that equilibrium assumptions and eutectic calculations are really representative. Assuming freezing rates were not very fast under the present experimental conditions maybe this is less of a problem. Nevertheless, a comment should be added in the text regarding the limitation of using eutectic equilibrium calculations for the frozen salts solutions.

Technical comment Table 3 - If authors are interested, previous study on 4-Nitrophenol photolysis in ice (Dubowski and Hoffmann, 2000), which showed similar quantum yield

as in solution, can be added to the table.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12063, 2010.

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