Response to Referee #2

The authors thank the referee for his or her comments.

Concerning the high gas-phase HCl and NH_3 concentrations used in our experiments:

High gas-phase concentrations were used in order to obtain an observable in our experiments over a reasonable period of time. HCl-induced disordering at the surface is a concern and the HCl-water phase diagram does indicate that at *equilibrium* a liquid-phase should be present for HCl vapour pressures used in the experiments. However, although very slight surface melting may have occurred in these experiments, we do not believe a liquid-layer was formed (i.e., equilibrium was not reached). This conclusion is supported by observations of acridine's fluorescence decay rate at the frozen freshwater surface during deposition of HCl(g) (Wren and Donaldson, *J. Phys. Chem. C.*, 116, 10171 – 10180, 2012). At the pure ice surface acridine's fluorescence is quenched compared to its fluorescence at the aqueous surface; deposition of HCl(g) to the pure ice surface does not lead to longer fluorescence lifetimes which would be indicative of a more liquid-like environment. The experiments described in this manuscript were performed in the same way. We also note that even taking into account possible surface melting, the main conclusion that frozen freshwater and frozen salt water surfaces exhibit different pH response holds.

The referee is concerned about harmine perturbing the chemical or physical state of the ice surface:

A very small concentration of harmine was used in these experiments (1×10^{-7} M). If *every* harmine molecule in the solution was present at the interface, the organic would form a loose monolayer there – such monolayers have not been found to be effective at blocking interfacial transport at the liquid surface~~.~~ We note that in our previous study using acridine as a dye (Wren and Donaldson, *J. Phys. Chem. C.*, 116, 10171 – 10180, 2012), deposition of HCl(g) to a frozen freshwater surface led to an sudden increase in the acridine fluorescence decay rate, indicating that the dye was sensing the deposition of acid. In that study measurements of final bulk pH indicated that the same amount of HCl had been delivered to liquid and frozen (pure water) samples, indicating that the dye was not preventing HCl uptake in the frozen case. In the present study we also find that final bulk pH is similar for frozen salt water and frozen freshwater experiments, again indicating that there is not a difference in harmine's blocking ability towards HCl between the two cases. In the experiments on frozen salt water or seawater, harmine is clearly sensitive to a change in pH due to deposition of HCl/NH_3.

Since the harmine concentration is low, we do not expect it to have a large influence on the surface acidic properties (although we cannot say definitely that there is no effect). We note that acridine and harmine have pKa's which differ by > 3, yet both dyes respond similarly when liquid and frozen freshwater samples are exposed to HCl(g)).(also see Wren and Donaldson, *J. Phys. Chem. C.*, 116, 10171 – 10180, 2012). We also note that the harmine 290/320 ratio follows the same trend as a function of initial pH (Figure 1b) on both the frozen freshwater and frozen salt water surface. If harmine had a strong influence on surface acidic properties at the surface one might not expect to see such good agreement (given that the surfaces present very different solvation environments).

The presence of harmine as an impurity at the frozen freshwater surface is expected to increase the extent of disorder in the ‘QLL’ over that of a truly pure ‘QLL’ (i.e., will slightly affect the physical structure). However, we believe that these low concentrations still leave the frozen freshwater surface in a state that is better described as a QLL than as a brine. This is supported by a) the results presented here which show a different behaviour for frozen freshwater vs. frozen saltwater and b) the harmine photolysis study by Kahan et al. (*ACP*, 10, 10917-10922, 2010) which shows a ‘tuning’ of the harmine photolysis rate from a ‘QLL rate’ to a ‘brine/aqueous rate’. The presence of harmine at the frozen saltwater or seawater surface should not influence the physical structure since a brine is expected to be present.

At the referee’s request, a few additional technical specific have been added to the abstract (mention glancing-angle LIF and harmine as a surface-active, pH-sensitive fluorescent probe).

The referee requests more experimental details concerning the use of harmine as an indicator to be given in the paper.

In our previous paper (Wren and Donaldson, *J. Phys. Chem. C.*, 116, 10171 – 10180, 2012) we describe in detail harmine’s photophysics and acid-base behaviour. We also describe the development and use of harmine as a pH indicator for aqueous and frozen surfaces. We refer the interested reader to this prior paper for these additional details. The focus of the current paper is not to present this technique as novel. We believe that details regarding harmine’s use as a pH indicator are described in the current manuscript to the extent to which is required for the purpose of this study (Section 3.1). Furthermore, the sensitivity of harmine to pH (via the harmine 290/320 ratio) is well illustrated by Figure 1b.

Figure 3 caption has been changed.