Geophysical Research Abstracts
Vol. 18, EGU2016-2206-1, 2016
EGU General Assembly 2016

A relationship between dissolved CO_2 and the non-volatile chemistry of rainwater.

Brian Durham (1) and Christian Pfrang (2)

(1) Research Laboratory for Archaeology, University of Oxford, UK (brian.durham@arch.ox.ac.uk), (2) Department of Chemistry, University of Reading, UK

Measurements of a volatile acid component in UK rainwater in 2009 implicated CO_2, and speculated 'a concentrating mechanism (that) could mean that this weakly soluble molecule is recycled at a faster rate than inferred by its Henry's Law constant'. Last year's EGU Presentation 2015-3386 confirmed that the 'saturated CO_2 content (of UK rainwater) is insignificant, the bulk transport being the volatile component'. However the atmospheric capture mechanism remains enigmatic. For pure water, improved temperature control has discounted the predicted upturn in the Henry coefficient for 450Pa CO_2 as the temperature approached freezing point (http://presentations.copernicus.org/EGU2015-3386_presentation.pptx), and the focus has therefore turned to rainwater chemistry. For a mid-range sample the Henry value was:
• significantly higher than pure water at 20'C;
• but decreasing with lower temperatures.

The higher Henry constant might suggest that, as an acid anhydride, CO_2 is subject to selective capture where cloud water is alkaline (terrestrial dust or marine aerosol). Analysis has however shown no simple relationship between $[CO_2]$aq and either acidity or conductivity of the carrier water. Seeking therefore a coherent distribution, stripped CO_2 was plotted against Δ[H+], from which this paper presents a tight wedge-shaped distribution of 263 UK rain/snow events. The inference is that $[CO_2]$aq is not related directly to [H+], but possibly to Group 1 and 2 cations from marine aerosol that are buffering the cloud water acidity.

By contrast, the unexpected decrease in CO_2 yield with lower temperatures proved to be an artefact of a progressively slower rate of de-gassing, cooler samples still equilibrating after 100 minutes. An ultrasound stripper is therefore being developed to speed the Henry measurements, and for reproducibility it is proposed to dilute a proprietary 'standard Atlantic sea water' to a representative range of conductivities, to be called 'standard rainwater'.

Any temptation to extrapolate from English results to address the global boundary layer is resisted pending ΔpH values from other stations, which are herewith invited in anticipation of IPCC AR6.