Phosphate as detected in Greenland firn

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Phosphorus (P) is an essential macronutrient for all living organisms. Phosphorus is often present in nature as the soluble phosphate ion PO_4^{3-} and has biological, terrestrial and marine emission sources. Thus PO_4^{3-} detected in ice cores has the potential to be an important tracer for biological activity in the past.

In this study a continuous and highly sensitive absorption method for detection of dissolved reactive phosphorus (DRP) in ice cores has been developed using a molybdate reagent and a 2 m liquid waveguide capillary cell (LWCC). DRP is the soluble form of the nutrient phosphorus, which reacts with molybdate. The method was optimized to meet the low concentrations of DRP in Greenland ice, with a depth resolution of approximately 2 cm and an analytical uncertainty of 1.1 nM (0.1 ppb) PO_4^{3-}. The method has been applied to segments of a shallow firn core from Northeast Greenland, indicating a mean concentration level of 2.74 nM (0.26 ppb) PO_4^{3-} for the period 1930-2005 with a standard deviation of 1.37 nM (0.13 ppb) PO_4^{3-} and values reaching as high as 10.52 nM (1 ppb) PO_4^{3-}. Similar levels were detected for the period 1771-1823. During volcanic eruptions the dissolved reactive phosphorus signal was enhanced, but within the range of observed natural variability. Based on impurity abundances, dust and biogenic particles were found the most likely sources of DRP deposited in North-east Greenland, while sea salts are unlikely to be a PO_4^{3-} source. Further we speculate that a number of high concentration spikes (>8.42 nM (0.8 ppb)) found during the late 20th century may be due to anthropogenic emission.

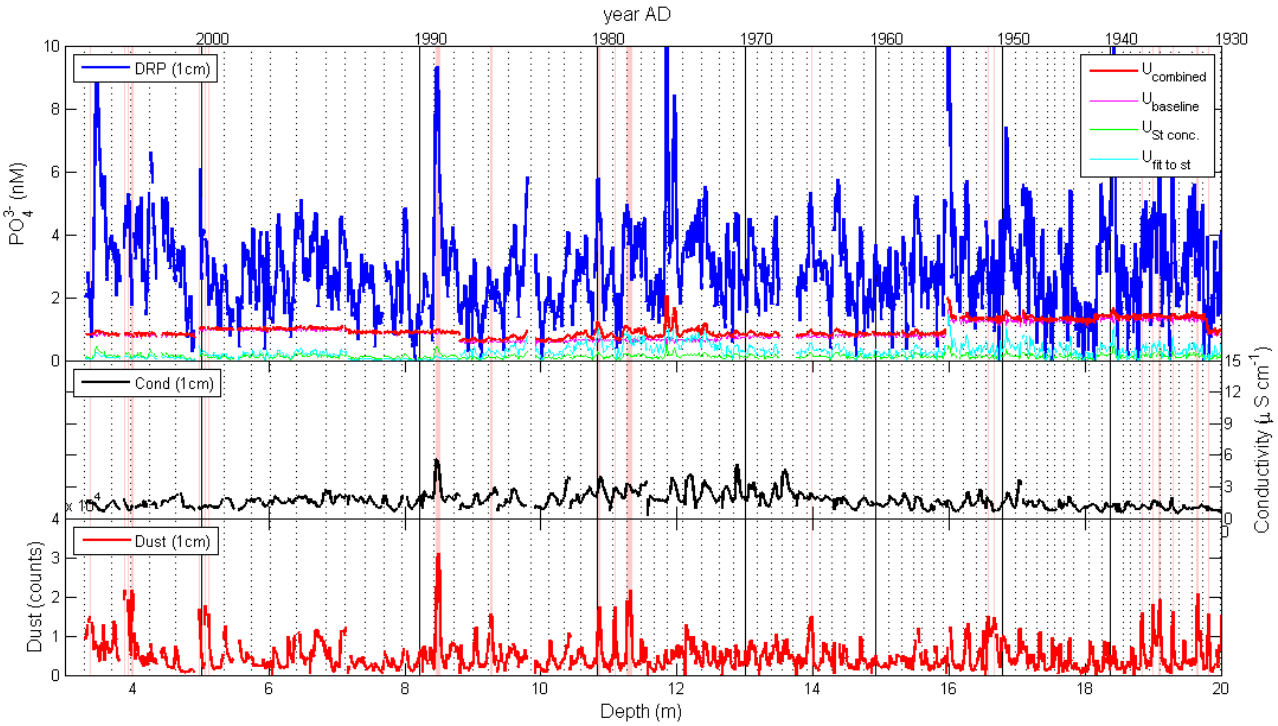

Figure 1. Top: DRP concentration on a depth scale with 1 cm smoothing as detected in the North East Greenland Ice Sheet (NEGIS) firn core (blue) together with the uncertainty (U) budget for DRP; magenta shows the uncertainty arising from the noise on the baseline, green from precision when preparing standards, cyan from the uncertainty on the fit used, and red is the combined uncertainty. Middle: Conductivity with a 1 cm smoothing. Bottom: Dust with a 1 cm smoothing. Vertical red bars indicate peaks of dust exceeding three standard deviations from the mean. Dotted vertical lines are annual layers as determined from Na^+ peaks.

Table 1. Estimated sources for DRP in the NEGIS firn core.

The anthropogenic estimate is based on Mahowald et al (2008).

Sources	DRP fraction (%)
Dust	4-100
Biogenic	4-38
Anthropogenic	0-10
Sea salt	0.3
Volcanoes	0

References

Kjær et al, *A continuous flow analysis method for determination of dissolved reactive phosphorus in ice cores*, Environmental Science & Research, submitted and accepted, 2013.

Mahowald et al., *Global distribution of atmospheric phosphorus sources, concentration and deposition rates, and anthropogenic impact*, Global Biogeochem. Cy., 22, 2008