



An atmospheric history of alkyl nitrates and alkanes in firn air: an indication of increasing NO_x in the Northern Hemisphere

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Firn air samples were collected from NGRIP, Greenland and analysed for a range of alkyl nitrates in the range C1 - C5 together with selected alkanes (ethane, propane, n-butane, i-butane). The mean age of air for these species at the base of the firn dates from the 1950s. The alkanes studied all increased substantially from the beginning of the record to the early 1990s, and have since declined, consistent with declining emissions in Europe and North America in the last decade. Propane and the butanes, for instance, approximately doubled in atmospheric mixing ratio to the 1990s. They have not, however, declined to the abundances prevalent in the 1950s. The C1 - C3 alkyl nitrates all appear to have been affected by chemical production in the lower firn, but isobutyl nitrate and the pentyl nitrates all present plausible atmospheric histories in the firn. Like the NMHCs the alkyl nitrates show increasing abundances since the 1950s, reaching a plateau in the early 1990s. In contrast to the alkanes, however, they increased several-fold during this period (factors of five or six), and in the last decade have declined more slowly, or in some cases remained constant. Assuming that the route to formation of alkyl nitrates is via the degradation of alkanes by hydroxyl radical, and subsequent reaction of the peroxy radicals with NO, then an increase in the abundance of Northern Hemispheric NO_x can be deduced.