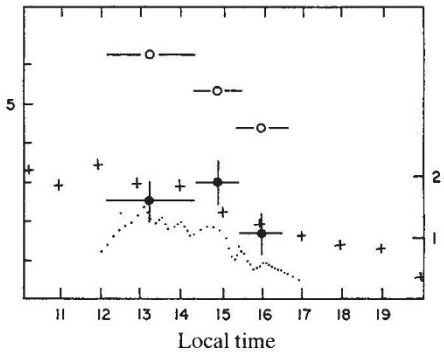
## Atmospheric chemistry

# Hunting tropospheric OH ions

*from D. Perner*

Is the self-cleansing capacity of the troposphere still adequate to cope with the ever-increasing amounts of emitted gases? Or could unchecked anthropogenic emissions eventually make populated areas uninhabitable? To measure accurately concentrations of the free hydroxyl radical (OH), generally regarded as the main agent for direct oxidation and for removal of substances from the atmosphere, has been a major challenge[1]. The article by Hard and co-workers on page 617 of this issue[5] describes measurements obtained by a promising new spectroscopic technique which should allow a test of whether




Comparison of the diurnal variation of measured OH concentrations $\times 10^6$ ml$^{-1}$ (left-hand scale) observed by optical absorption[8] on 19 May 1983 at Deuselbach (black circles), and by laser-induced fluorescence[5] on 18 June 1985 at Portland (crosses). Also shown are the $O_3$ photolysis frequency $\times 10^{-5}$ s$^{-1}$ (right-hand scale; dotted line) and the calculated OH concentration (open circles), both for Deuselbach[8].

our understanding of atmospheric photochemistry is consistent with measured OH concentrations.

It is only since the early 1970s that the central role of the OH free radical in the troposphere has become apparent. In 1969 Weinstock[6] ascribed the strong variability of carbon monoxide in the troposphere to the action of OH radicals, but he could not identify their source. Two years later, Levy[7] found that not all of the Sun's ultraviolet light, which produces excited oxygen atoms from ambient ozone, was filtered out by the stratosphere. Because this excited oxygen is the primary intermediate for OH formation, an appreciable source of OH therefore exists in the troposphere.

Although highly labile, OH does not react with any of the major atmospheric components, so it can exert its full oxidative power on trace gases such as methane, carbon monoxide and methyl chloride, which are eventually converted into carbon dioxide, water and other stable products that are washed out of the atmosphere. This process has prevented trace compounds from building up in the atmosphere over the millenia. OH is important because it is regenerated in these oxidation processes: in the free atmosphere, typically up to five oxidation reactions are initiated by OH before it is scavenged. Despite this amplification of OH, fast chemical reactions keep its ambient concentration quite low, to about a few million molecules per millimetre in sunlit air. It is also commonly accepted that the concentrations at night are considerably below those in the daytime.

Several *in situ* techniques for measuring OH concentrations are presently in use. Radiolabelled products, such as $^{14}CO_2$ formed from $^{14}CO$ by the OH reaction, can be measured with high-sensitivity or spectroscopic methods to probe the OH concentrations directly[1-3]. Hard *et al.*[5] apply laser-induced fluorescence at low pressure in a manner that excludes ambient light from the detector. In this way difficulties previously found using this technique are circumvented and the instrument can be converted easily for aircraft measurements.

The midday OH concentrations found in Portland by Hard *et al.*[5] can be compared with similar observations in Deuselbach by my own group obtained by long-path optical absorption (see figure). Whereas in Deuselbach the OH signal disappears at 1700 h, the OH in Portland extends fairly late into the evening and, surprisingly, is found at night. The reason for this unexpected and interesting observation is unknown. Other types of data from Portland are not detailed enough to calculate a model of the OH distribution. In contrast, other types of data from Deuselbach predict much higher OH concentrations than are found experimentally there. Thus the theoretical description at Deuselbach cannot be applied.

I still believe that direct evidence for free tropospheric OH, preferably by spectroscopy, is needed. Simultaneous measurements of all species and parameters in the OH photochemical cycle, together with the OH measurements, are now a prerequisite to test our[5] atmospheric theory. Investigations of various air masses should be made to represent the whole of the troposphere, and then we could distinguish between the importance of homogeneous gas-phase chemistry and heterogeneous processes taking place at the surface of aerosols or in droplets. Only then shall we learn whether the observed increase in concentration of climate-effective gases like methane is caused in part by a decline in atmospheric self-cleansing by OH. □

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*D. Perner is in the Department of Atmospheric Chemistry at the Max Planck Institute for Chemistry, Postfach 3060, D-6500 Mainz, FRG.*

## Archaeology

# Japanese agricultural beginnings

*from Gina L. Barnes*

AGRICULTURE in the Japanese islands was long thought to begin with the importation of wet rice technology from the continent at around 300 BC, an event taken to mark the transition from a hunting and gathering economy in the postglacial Jomon period to a period of settled agricultural communities. But this traditional view has been thoroughly overturned in the past ten years with discovery of the remains of many cultivated plants — including rice — from Jomon sites. The recovery of buckwheat pollen from the Ubuka bog in southwestern Japan, reported on page 632 of this issue, provides the strikingly early date of 6,600±75 years before present (BP) for buckwheat cultivation, paralleled only by the finds of beans and gourd at the Torihama site which are dated to 5,000–3,500 BC. If these data become widely accepted, they may lead to a substantial revision of our ideas about the pattern of human settlement during this period.

Models allowing flexibility in determining the role of plants in the different regional and temporal complexes of the Jomon period have already been developed[3,4] and a major advance has been the correlation of population densities with forest and fishery zones[5-7]. This correlation indicates that the population occupying the southwestern evergreen oak–laurel forest at low density was less dependent on hunted animals — scarce in such a forest regime — and therefore more dependent on plant foods. The abundant floral remains at Torihama from the early Jomon period support this idea and