# Stalking the Elusive Atmospheric Hydroxyl Radical

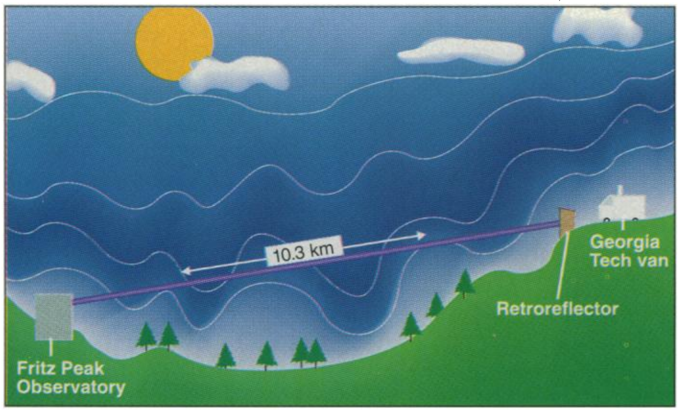
### William H. Brune

The hydroxyl radical has long been the Howard Hughes of atmospheric chemistry. It is elusive but important, and the subject of much speculation. Now, measurements of its abundance by two quite dissimilar methods reported on page 1187 of this issue (*1*) show us that we might get acquainted with it after all. When informally intercompared last summer in the Colorado Rockies, these methods gave surprisingly similar numbers for the hydroxyl abundances, and eye-opening disagreements with theoretical predictions.

Atmospheric chemists have tried a half dozen ways to measure the hydroxyl abundances over the last 20 years. None has been completely successful (*2*). Usually some interfering signals, such as those from organic molecules or hydroxyl generated during detection by laser-induced fluorescence, swamped the small signal from atmospheric hydroxyl. The measurements are so difficult because the hydroxyl abundances are so low—only a few tenths of a part per trillion. Few instruments with this sort of sensitivity and selectivity exist for any atmospheric chemical radical.

The informal intercomparison in the Colorado Rockies last summer signals the beginning of a new era in hydroxyl measurements. First, the two methods use entirely different physical principles. If their measurements agree, then we have greater confidence that each is free of major problems, and that each is measuring atmospheric hydroxyl. The long-path absorption method of Mount (*3*) relies entirely upon the absorption spectroscopy of the hydroxyl radical. Sending laser light across a wide mountain valley, Mount uses Beer's Law to convert the small, observed absorptions (a few times $10^{-4}$) into absolute hydroxyl abundances. This method is absolute, but is bothered by small absorptions by other trace molecules. The local, or point, measurement method of Eisele and co-workers (*4*) relies entirely on the chemistry of the hydroxyl radical. They use chemical reactions to convert hydroxyl to sulfate, which they then selectively ionize and detect with a mass spectrometer. This method lacks the spectral fingerprint of the hydroxyl radical, but it is more sensitive.

The informal intercomparison is also important because these two methods are more sensitive and specific than their predecessors. Both can detect hydroxyl abundances far below the typical values for midday. Detection limits for hydroxyl radicals are about $5 \times 10^5$ cm$^{-3}$ for detection times of a few minutes for the long-path measurement and about $1 \times 10^5$ cm$^{-3}$ in a few minutes for the ion-assisted measurement. Both limits are significantly below the "typical" midday values of $5 \times 10^6$ cm$^{-3}$. These sensitivities are sufficient to test the photochemical theories of the lower atmosphere.



**Measurement of hydroxyl with two different methods.** The long-path and the local, ion-assisted methods generally agree despite the great differences in air sampling by the two methods. Hydroxyl abundances are small near the surface and increase with height up to a few kilometers, where they again decrease.

These two techniques sample the hydroxyl abundances on vastly different spatial scales: for the long-path method, over 10.3 km; for the ion-assisted method, over a few centimeters. And yet, when the ion-assisted instrument was set at one end of the long path, the hydroxyl abundances that Mount and Eisele derived from their measurements generally agreed to within a factor of 2. Mount and Eisele even measured the same diurnal changes for hydroxyl. Of course, the long-path and ion-assisted measurements did not always agree. On several occasions, the ion-assisted measurements were lower by a factor of 2 to 3.

Such differences are not surprising when we consider how ephemeral the hydroxyl radical is (*5*). It is produced when ultraviolet sunlight decomposes ozone into molecular oxygen and energetically excited oxygen atoms. These oxygen atoms mostly lose their excess energy as heat, but a small fraction reacts with water vapor to form two hydroxyl molecules. The hydroxyl radical is destroyed by reactions with a large number of other trace gases and by collisions with the ground, plants, and other surfaces. These reactants are so numerous that the hydroxyl radical disappears within a few seconds in the shadow of a thick cloud passing overhead. Thus, differences in the sunlight, the number and type of reactants, and the proximity to surfaces for the long-path and local, ion-assisted methods will inevitably lead to differences in the measured abundances of hydroxyl.

The intercomparison between these measured hydroxyl abundances and the predictions of photochemical models is not so encouraging. Predicted abundances of hydroxyl were usually larger than the observed values by much more than the uncertainty in the measurements (*6*). Further, the observed diurnal variation of hydroxyl was much less than predicted, as if some reactant was limiting the peak value of the hydroxyl abundance. Mount and Eisele believe that some unmeasured and unknown hydrocarbon, emitted from the local forests, chews up increasing amounts of hydroxyl as the day passes.

Before this intercomparison, we had more confidence in the hydroxyl abundances predicted by computer models than those determined by measurements (*7*). Now, in the presence of significant measurements, we see that the current theoretical description of the chemistry in the lower atmosphere may need revision. But these measurements of hydroxyl are heavily influenced by the local environment. Can they still tell us something about the global abundances of hydroxyl, discussed by Thompson on page 1157 of this issue (*8*), that have the greatest effect on both global warming and future stratospheric ozone depletion?

We do not yet have the answer to this question. However, this informal intercomparison has shown that the tools to make significant hydroxyl measurements now exist. We now need to measure hydroxyl, simultaneously with everything that might affect hydroxyl, in environments such as the Colorado Rockies. We also need to sample other environments, particularly

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the free atmosphere, away from the influences of the earth's surface. From all of these measurements will come an understanding of the processes that control hydroxyl and determine the oxidizing capacity of the atmosphere.

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# The Continuing Case of the Florida Dentist

Temple F. Smith and Michael S. Waterman

Applications of DNA fingerprinting or typing are becoming increasingly common and diverse. A suspect can be convicted or set free on the basis of a "fingerprint" of DNA found at a crime scene. In a recent dramatic case, the Nazi war criminal Josef Mengele of the notorious Auschwitz concentration camp was declared to have been dead for more than a decade on the basis of a DNA fingerprint match between a set of Brazilian bones and a sample from his living son. This is an example of the use of DNA fingerprinting to establish relationships, in this case by paternity testing. General applications of DNA fingerprinting in pediatric practice range from paternal identification through genetic disease diagnoses to child abuse verification (*1*). In this issue of *Science* Ou *et al.* (*2*) present an analysis of the viral DNAs associated with the alleged human immunodeficiency virus type 1 (HIV-1) infection of a number of patients by their Florida dentist.

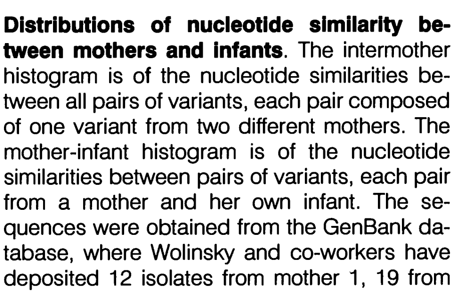
These uses of molecular data raise a multitude of important issues, both scientific and ethical. There are also major unresolved issues as to the levels of statistical and scientific reliability appropriate for deciding public policy or for use in our judicial system. In 1989 Lander (*3*) argued that new experimental standards must be defined for DNA data use in judicial cases but did not directly address the statistical issues. A recent report of the National Academy of Sciences Panel on DNA and Forensic Science, headed by Victor McKusick of Johns Hopkins Hospital (*4*), addresses these and related issues. These questions must be addressed by the scientific community because science is and will continue to be used to formulate public policy and to form judicial decisions. Quite often scientific data and conclusions are used by those unfamiliar with its limitations.

The majority of comparative DNA sequence studies have as their conclusion the generation of scientific inferences. It is ideal if such inferences are supported by overwhelming statistical evidence. However, under the assumption of eventual experimental testing of these inferences, those supported by evidence of even marginal statistical significance can be quite valuable, particularly when deciding which experiment to perform next among the myriad possible experiments. In other situations, statistics play an important but less well-defined role. For example, in the public policy arena, estimates of statistical significance are folded into risk-cost-benefit analyses, cost-effectiveness studies, and policy analyses. Here the links between science, statistics, and conclusions can become very obscure. In these areas, there is not always a guarantee of timely rejection of incorrect inferences as a result of experimentation nor is there an accepted criterion for statistical significance. The statistical significance used by the public and many agencies to recommend life-style changes often is not extremely strong, particularly as it may relate to cancer. One should recall that the great statistician and biologist R. A. Fisher never accepted even the evidence linking smoking and lung cancer; the public certainty has come from evidence accumulated since Fisher's death. However, the analyses of HIV-1 transmission have provided sufficient statistical evidence for most nations to spend considerable money on research, to recommend the wide use of condoms, and to support the use of gloves by all medical personnel.

The statistical criteria used in scientific inference or in public policy generation are distinct from those for setting new legal precedents or for civil or criminal courts. Legal situations require the highest statistical significance to generate a verdict beyond a reasonable doubt! The obvious potential forensic utility of various molecular techniques could be lost if their early judicial use is inconclusive or improper. The concern here is not academic as exemplified by Ou *et al.* (*2*) in which statistical analyses of the alleged HIV-1 infection of patients by their dentist were used to conclude that, for at least five of his patients, the dentist was the most likely source of the infection. The work can influence pending insurance cases and public health policies and has already been involved in a Florida court process. The court delayed certain actions until the publication decision of this journal and until all of the data were made public (*5*).

Not only were the authors likely to be quoted or called by the court, but the reviewers were under some additional pressure. A News & Comment piece (*5*) even appeared before the review process was complete. This was due, in part, to the fact that some of the data in the present analysis had been used in an earlier preliminary study (*6*) and that an early copy of Ou *et al.* (*2*) had been obtained through the Freedom of Information Act. In addition, there was some delay in making available the entire data set to all parties concerned.

Thus, it is clearly possible for data, a manuscript, and even the review process to become entangled in the legal process. When there is potential for legal implica-



**Distributions of nucleotide similarity between mothers and infants.** The intermother histogram is of the nucleotide similarities between all pairs of variants, each pair composed of one variant from two different mothers. The mother-infant histogram is of the nucleotide similarities between pairs of variants, each pair from a mother and her own infant. The sequences were obtained from the GenBank database, where Wolinsky and co-workers have deposited 12 isolates from mother 1, 19 from mother 2, and 23 from mother 3, along with 21 isolates for the infant of mother 1, 13 for that of mother 2, and 27 for that of mother 3.

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