

FURTHER COMMENTS

In their reply, Hov *et al.* mention the problem of absolute calibration and the comparability of data from different groups as a possible explanation of the different values found for propane. Their results are based on commercial standards whereas our calibration is based upon mixtures prepared by static dilution of the pure propane in synthetic air in our laboratory. I fully agree that a thorough intercomparison of the calibrations and the measuring techniques of the various groups is needed. However, I have some reservations against the use of commercial standards as bases for an absolute calibration.

Nearly all published nonmethane hydrocarbon (NMHC) data in the remote troposphere show that, on a carbon atom basis, ethane is the most abundant NMHC (cf. Bonsang and Lambert, 1985; Greenberg and Zimmerman, 1984; Rudolph and Ehhalt, 1981; Rudolph 1988; Singh *et al.*, 1988). Our measurements indicate that this also holds for the Norwegian Arctic. However, Hov *et al.* observed that propane is the most abundant NMHC in this region. Global emission data (cf. Ehhalt and Rudolph, 1984) and the atmospheric lifetimes of light NMHC (cf. Rudolph and Ehhalt, 1981) require that on the average ethane should be the most abundant NMHC in the remote troposphere. Thus the two different calibrations give a significantly different picture of the role of propane in the Norwegian Arctic. In order to decide whether the Arctic propane mixing ratios fit into the general global picture or require some unusual alkane emission patterns we need a reasonable estimate of the accuracy of the different calibrations. Comparability alone cannot answer this question.

Hov *et al.* used two different commercial standards and found propane values differing by roughly 50%. However, the use of any of the two standards gives tropospheric propane mixing ratios which are significantly higher than our results. In May 1987 we participated in an intercalibration experiment organized by the NOAA Atlantic Oceanographic and Meteorological Laboratory, Miami, Florida. As part of this exercise, samples from a tank with pressurized oceanic air were distributed and analyzed by nine different laboratories. The relative standard deviation of all nine propane

measurements was 35.3% and seven of the nine laboratories differed by less than 20% from the average of 0.4 ppbC. Our results agreed within less than 5% with the average.

This indicates that the unusually high propane values reported by Hov *et al.* are probably due to the use of a commercial calibration gas which differs by roughly a factor of two (or 1.5 for the second commercial standard) from the average calibration of nine independent laboratories. Thus a reliable absolute calibration is not just a matter of comparability between different laboratories and the use of a commercial standard without any comparison with other independent calibrations cannot be recommended.

In my opinion the suggestion of Hov *et al.* to use commercial calibration gases in order to achieve comparability of the calibrations needs to be modified. If a commercial standard is used by all groups *in addition* to an absolute calibration this might be very useful to improve the comparability between NMHC data from different groups.

However there are a number of technical problems which have to be solved before any commercial standard might be useful as reference gas. In general the NMHC mixing ratios in commercial gas standards are in the ppm range, about 3–4 orders of magnitude above the usual tropospheric mixing ratios. Thus a reliable and standardized procedure for the extrapolation from a ppm standard to ppb and sub ppb levels is needed in order to ascertain comparability of data from different groups. Also there are several manufacturers who offer gas mixtures with defined NMHC concentrations and the different groups have to agree on the use of a single standard. Finally the supplier has to guarantee that there will be no changes in the production or calibration procedure for the chosen standards.

There are several groups in Europe with independent absolute calibrations which have been compared internationally. Although we are still far from having an established common NMHC calibration, I would suggest that groups without their own calibration should try to connect their calibration to those of groups with their own absolute calibration. In view of the various problems connected with the use of the presently available commercial NMHC standards I would not recommend the general use of these standards as a basis for an absolute calibration for published NMHC data.

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