

Whole Air Sampling at Barrow, Alaska

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The University of California-Irvine (UCI) has been collecting whole air samples at the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) station at Barrow, Alaska, since April 1983. The Barrow measurements are the northernmost sampling site of the UCI global CH₄ monitoring network that extends from 71°N to 47°S. The UCI and CMDL CH₄ networks have a second co-located sampling site in Samoa.

In the UCI sampling strategy, approximately 60-80 whole air samples are collected over a 3-wk period in 40-45 locations four times a year (usually March, June, September, and December). Of these samples, four or five are collected in Barrow, usually over a 2-3 day period. The air samples are collected in conditioned, evacuated 2-L stainless steel canisters equipped with a single stainless steel bellows valve. During sampling, the canister is filled to ambient pressure over a period of about 1 minute. At the end of the collection period the sampling canisters are returned to the UCI laboratory for analysis.

The CH₄ mixing ratio within an air sample is determined by gas chromatography (HP-5890A) with flame ionization detection. The CH₄ mixing ratios are reported for dry air relative to primary standards purchased in 1977 and a National Institute of Standards and Technology (NIST) (formerly known as the National Bureau of Standards (NBS)) standard purchased in August 1982. The uncertainty in the NIST standard is $\pm 1\%$. The analytical precision is determined from intersample comparisons that are obtained by alternating measurements of secondary standards with aliquots from an individual air sample. The UCI analytical precision was 3 ppbv in the 1980s and is currently better than 2 ppbv. Data points are individually inspected, and points that do not represent remote values are removed from further analysis.

The UCI global CH₄ monitoring program complements the fixed station network of the CMDL program. The UCI sampling strategy emphasizes intense latitudinal sampling over a short (3-wk) period while sacrificing the knowledge and statistical confidence gained from multiple or continual measurements at individual sites. The UCI sampling locations are not fixed, and sampling personnel scout out the best location and time for a remote air sample according to the prevailing physical and meteorological conditions. As a result, the method has the flexibility to easily switch sampling sites if local contamination is suspected.

Individual CH₄ mixing ratios measured at Barrow by UCI over the 2-yr period from March 1998 to December 1999 are shown in Figure 1. Unlike the other sites in the UCI monitoring network, the Barrow and Samoa sampling locations are fixed at the CMDL stations. As a result, the CH₄ mixing ratios measured at these sites are sometimes elevated as a result of local contamination. At Barrow local contamination can occur when the prevailing wind is from the direction of town rather than from the ocean or tundra. During 1998-1999 the measurements collected in September 1998 and March 1999 were elevated as a result of local contamination and have not been included in

Figure 1. Indeed, the CH₄ mixing ratio exceeded 2 ppmv in two of the UCI samples collected in September 1998. The CMDL measurements were similarly elevated at this time, confirming that the enhancements were real and not a result of measurement error.

The remaining six sets of seasonal data generally show very low variability within a given season (Figure 1). The measurement precision (2 ppbv) is roughly the same size as the data points that have been plotted, and the difference among the data points within a given season represents real variability, rather than measurement error. The mixing ratios over the 2-yr period show a characteristic seasonal pattern with a summertime minimum and a winter maximum (Figure 1).

The CMDL and UCI networks are two of just three global monitoring networks for tropospheric CH₄. The overlapping sampling at Barrow provides a valuable opportunity for measurement intercomparison. Over the years we have found that the UCI CH₄ mixing ratios typically exceed those of the CMDL network by ~ 20 ppbv. The difference is caused by an offset in the calibration scales used by the two groups. A scaling factor of 0.989 would make the UCI measurements agree with the CMDL values. Many other groups require similar scaling factors, again as a result of different calibration scales that are used (e.g., Atmospheric Environment Service (AES) Canada, Institute of Atmospheric Chemistry (IAC) China, Ente per le Nuove Tecnologie, l'Energia e l'Ambiente (ENEA) Italy, National Institute for Water and Atmospheric Research (NIWA) New Zealand; see <http://www.cmdl.noaa.gov/ccgg/globalview/ch4/methods.html>).

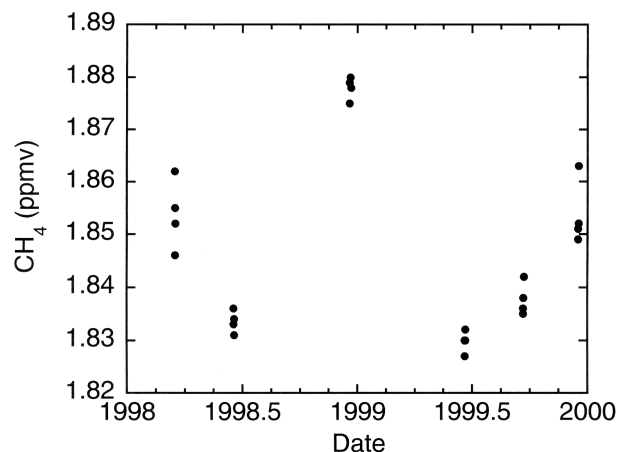


Fig. 1. Methane mixing ratios (ppmv) measured by the University of California-Irvine (UCI) at the NOAA CMDL station in Barrow, Alaska, between March 1998 and December 1999. Mixing ratios measured in September 1998 and March 1999 were enhanced by local contamination and have not been included in the graph.