**Direct measurements of atmospheric CH4 mole fractions:**

**Introduction:**

This section focuses on high-precision, long-term measurements of atmospheric CH4 dry air mole fractions using instruments calibrated with SI-traceable standards. These measurements are in contrast to remotely-sensed CH4 retrievals, which can not be calibrated, only evaluated by indirect comparisons with in situ measurements and models.

Measurements of CH4 at background sites that sample well-mixed air representative of large volumes of the atmosphere are useful for constraining the global CH4 budget at large spatial scales (global, hemispheric, and continental) and providing accurate estimates of the increase in radiative forcing since the pre-industrial era. Although the first reports of CH4 detection in the atmosphere were in the French literature in the 1830s (as described in Reeburgh, 2004), the first modern measurements, made by looking at solar IR absorption, were by Migeotte (1948a,b). Systematic measurements of atmospheric CH4’s spatial and temporal distribution at remote air sampling sites began in the late-1970s and early-1980s, and many of those programs continue to measure CH4 today.

In 2014, atmospheric CH4 measurements are used for much more than assessment of trends; they provide “top-down” constraints on the global CH4 budget of emissions and sinks. Data from many sources are often combined, and their spatial and temporal gradients are exploited by a chemical transport model (CTM) to infer fluxes by region and source type. For this to work, the data must meet stringent criteria for quality. The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) program provides a framework in which measurement laboratories and data users have developed a quality assurance framework to ensure the data are scientifically useful. These quality assurance targets, given in a list of recommendations and measurement compatibility goals, are updated every 2 years at meetings of the GHG measurement community. Coordination also occurs at finer level, for example within Europe under the Integrated non-CO2 Greenhouse gas Observing System (InGOS). Their goal is to harmonize current and historical data from many labs across Europe (http://www.ingos-infrastructure.eu/).

This section focusses on long-term measurement programs with data that are published or available from a data center, for example the World Data Center for Greenhouse gases (WDCGG; http://ds.data.jma.go.jp/gmd/wdcgg/) maintained by the Japan Meteorological Agency as a contribution to the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) program.

*Standard scales for atmospheric CH4 measurements:*

Direct measurements of atmospheric CH4, either from discrete air samples or in situ, are typically made using gas chromatography with flame ionization detection or a spectroscopic method. Both are relative techniques and their response to CH4 needs to be calibrated frequently to meet scientific requirements of precision and accuracy. WMO GAW recommends that all laboratories contributing CH4 measurements to GAW use a common standard scale maintained by a GAW-designated Central Calibration Laboratory (CCL). The WMO mole fraction scale for CH4 is maintained by NOAA ESRL GMD (Dlugokencky et al., 2005). Other standard scales are in use, and they are sometimes linked to the WMO scale through a conversion factor. WMO GAW organizes round robin comparisons of standards every 4 or 5 years through a World Calibration Center (NOAA) and makes results available through a web interface (http://www.esrl.noaa.gov/gmd/ccgg/wmorr/results.php). Results of these and other less-formal comparisons are used to calculate conversion factors to convert data from one scale to another. For example, a table of conversion factors to the WMO CH4 mole fraction scale is given for GLOBALVIEW-CH4 (<http://www.esrl.noaa.gov/gmd/ccgg/globalview/ch4/ch4_method.html>). In many cases though, no direct link exists between scales. Air samples are always either dried or measured wet and corrected to eliminate the dilution effects of water vapor, especially relative to dry standards. Methane measurements are reported as “amount of substance” (Schwartz and Warneck, 1995) with units of dry-air “mole fraction”, in this case nmol mol‑1, typically abbreviated “ppb” for parts per billion by moles, or µmol mol‑1, typically abbreviated “ppm” for parts per million by moles.

*Sampling strategies:*

There are two major sampling strategies in use for direct measurements of atmospheric CH4, discrete air samples collected in flasks (typically glass or metal) and measured at a base laboratory, and use of a quasi-continuous in situ analyzer at the sampling site. Discrete sampling has key advantages: 1. Samples can be collected with a portable, battery-powered air sampler in locations where line power is not available. 2. Samples can then be measured for multiple species, including isotopic composition. 3. Samples from an entire air sampling network are measured on a common analytical system with a common set of standards, which assures measurements that are internally consistent. Major disadvantages are: 1. Sampling is usually infrequent (e.g., weekly), but this is acceptable at background sampling sites where short-term variability in CH4 is relatively small. 2. The integrity of the air sample may be compromised by storage, either by interaction of air with the flask walls or preferential diffusion of certain species relative to others through O-rings resulting from different permeation rates (Sturm et al., 2004). This latter effect can be minimized by using appropriate materials for the flasks and sampling pressures close to ambient, since diffusion rates through semi-permeable membranes are proportional to the concentration gradient across the O-ring. Laboratories test the integrity of sample canisters over time spans important to their programs by filling a suite of flasks from a cylinder of dry natural air that is well calibrated for CH4, then analyzing groups of flasks after various storage times and comparing the result with the assigned value of the cylinder. In situ analyzers offer high-frequency measurements (up to 1 Hz with reasonable precision, but more typically averaged to 1 min or longer) and lack of gas storage effects. These measurements contain information on short-term variability and diurnal cycles, which are useful for characterizing a sampling site. Disadvantages are: 1. There is a relatively large initial cost of the analyzer, standards, data acquisition system, and gas handling system, which multiplies by the number of measurement sites. 2. It must be engineered to operate with autonomously. 3. Standards must be accurately propagated to each site to avoid intra-network biases. 4. Skilled technicians are normally needed nearby the measurement site to help maintain the systems. Spectroscopic methods using off-axis, integrated cavity optical spectroscopy or cavity ring-down spectroscopy have helped lower technological barriers to in situ measurements while ensuring high quality measurements, but at significantly greater short-term cost than a GC.

**Surface CH4 measurements:**

Measurement programs with the longest histories were designed to determine trends in atmospheric CH4 burden and to provide information that constrains the large scale features of CH4’s global budget. Therefore, measurement sites were chosen in remote locations, so sampled air would represent large well-mixed volumes of the atmosphere and not be influenced by local or regional emissions and sinks. In a paper describing the atmospheric CH4 cycle, Ehhalt (1974) summarized early background measurements of CH4 and its spatial distribution. Khalil et al. (1989) summarized atmospheric CH4 measurements from the 1960s and 1970s to try to quantify trends. Older measurements summarized in these papers are difficult to compare with modern measurements (i.e., since the late-1970s), because standard scales used are often not traceable to those used by modern measurement programs.

Measurement programs that began during the late-1970s and early-1980s demonstrated that the global atmospheric burden of CH4 was increasing at a relative rate of 1-2% yr-1 (Rasmussen and Khalil, 1981; Fraser et al., 1981; Blake et al., 1982; Khalil and Rasmussen, 1983; Fraser et al., 1984; Fraser et al., 1986). Some of these measurement programs also determined the spatial patterns in atmospheric CH4 distribution, which is a useful constraint on the global budget of emissions and sinks. Blake and Rowland (1988; also Blake et al., 1982) determined the global atmospheric CH4 burden and its distribution by sampling through the Pacific seasonally across a wide range of latitude (71°N to 47°S). These infrequent measurements made it difficult to characterize the CH4 seasonal cycle. Khalil and Rasmussen (1983) determined globally averaged surface CH4 and its spatial distribution from 7 surface sites, and used the observations to assess methane’s lifetime and total global emissions. Their measurement program is no longer active. Long-term monitoring of CH4 and other components of atmospheric composition is important for climate and air quality studies, so there was a clear role for a government agency to start observations to ensure continuity. To meet this need, NOAA began measuring atmospheric CH4 in air samples collected from its cooperative global air sampling network in 1983 (Steele et al., 1987). At that time, their network consisted of 23 background air sampling sites, where observed CH4 was representative of large well-mixed volumes of the atmosphere. In the early-1990s, NOAA’s network was expanded to include continental sites with regional influences on observed CH4. Measurements are on-going in 2014, although the network of sites varies over time. Samples are collected about weekly in pairs with a portable sampling system and returned to Boulder for analysis of CH4 and a suite of other species. The sampling and measurement methods were described in detail by Steele et al. (1984) and Dlugokencky et al. (1994). Global CH4 averages have also been inferred from quasi-continuous, in situ measurements at 5 sites by the Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment (GAGE/AGAGE) program (Cunnold et al., 2002) using a 12-box model.

Observations of atmospheric CH4 provide many important constraints on CH4’s global budget (Cicerone and Oremland, 1988). Determinations of globally averaged CH4 at Earth’s surface (Figure 1a) are used to calculate the atmospheric burden, or total mass of CH4 in the atmosphere, with a conversion factor that accounts for the decrease in CH4 with altitude (e.g., 2.767 Tg CH4 ppb-1 (Fung et al., 1991) or 2.75 Tg CH4 ppb-1 (Prather et al., 2012). Methane’s rate of increase is a measure of the imbalance between emissions and loss processes. With an estimate of CH4’s atmospheric residence time (~9 yr), the burden and growth rate can be used to calculate total annual global emissions (Figure 2). Interannual variations in growth rate can be used to test understanding of specific source or sink processes. Observed seasonal cycles and spatial gradients (Figure 3) constrain the seasonality and spatial distribution of processes that affect atmospheric CH4, often using atmospheric chemical transport models (see section on inverse modeling). Atmospheric CH4’s trend, over both the long-term and short-term (i.e., interannual variability), contains important information about how CH4’s global budget is evolving over time.

*Long-term global trend analysis:* Steele et al. (1992) reported that the CH4 growth rate was decreasing from 1983-1990, and the cause was decreasing emissions at 30-90°N. Dlugokencky et al. (1998) showed that the decreasing growth rate reported by Steele et al. (1992) continued from 1984-1996, and, assuming no trend in CH4 lifetime, it could be explained by constant emissions and an approach to steady state atmospheric CH4 burden. This pattern of constant emissions lasted from 1984-2006, during which atmospheric CH4 growth rate slowed and its burden was nearly constant from 1999-2006. In 2007, CH4 began increasing again (Rigby et al., 2008; Dlugokencky et al., 2009) as a result of increasing emissions (Figure 2; update of Dlugokencky et al. (1998; 2003)). While total global emissions remained constant from 1984-2006, emissions from specific sources, e.g., natural gas from venting, likely decreased (Simpson et al., 2012; Aiden et al., 2011). But, unless methane’s lifetime were changing, those decreases needed to be balanced by increased emissions from other sources.

*Interannual variability in CH4 growth rate:* Since 1990, there have been repeated significant variations in globally averaged CH4 growth rate (Figure 1b) caused by a variety of processes. In 1991, CH4 growth rate increased, particularly in the tropics; the increase was also seen in measurements of CO and it was caused by a perturbation to atmospheric photochemistry. Dlugokencky et al. (1996) showed that ash and SO2 emitted during the eruption, and subsequent sulfate aerosol as the SO2 was oxidized, reduced tropospheric UV radiation flux at 290-330 nm resulted in decreased tropical [OH] and a anomalous increase in CH4 growth rate. Almost immediately after the eruption of Mt. Pinatubo, CH4 growth rate decreased. The causes of this seemed to change the trajectory of the future atmospheric CH4 burden. Dlugokencky et al. (1994) reported that the most likely cause was decreased anthropogenic emissions from the former Soviet Union. This source, rather than emissions from wetlands or a temporary increase in chemical sink, is most consistent with permanent decreases in the observed north-to-south difference in CH4 (Dlugokencky et al., 2003). A large increase in CH4 growth rate occurred during 1998 (Dlugokencky et al., 2001; Simpson et al., 2002); changes in wetland and biomass burning emissions during the extreme El Niño of 1997/1998 are likely causes (Langenfelds et al., 2002).

*Continuous measurements:* There are many national programs that measure atmospheric CH4 quasi-continuously at atmospheric observatories. Publications describing measurements and sampling site usually analyze the data for trends, seasonal cycles, and estimates of regional emissions within a model framework. These studies contrast to earlier studies that investigate CH4’s global budget. In the Northern Hemisphere, CH4 is monitored quasi-continuously by NOAA at Mauna Loa and Barrow Observatories (Dlugokencky et al., 1995). The main uses of the data are as quality control and estimating uncertainties for discrete sample measurements from NOAA’s cooperative global air sampling network. Artuso et al. (2007) described measurements from Lampadusa, Italy, an island in the Mediterranean. They see strong variability in CH4 with varying air mass trajectory, which demonstrates the usefulness of continuous measurements combined with particle dispersion models for estimating regional scale measurements. Environment Canada started continuous measurements of CH4 at the baseline observatory at Alert, Nunavut, Canada in 1992 (Worthy et al., 1998). They have expanded measurements in Canada to 21 sites in 2014 to help quantify emissions from natural and anthropogenic sources in the Arctic using top-down methods. In Asia, continuous measurements are operated by JMA at Ryori (1991-2014), Minamitorashima (1994-2014), and Yonagunijima (1998-2014) and described by Tsutsumi et al. (2006). The Japanese National Institute for Environmental Studies (NIES) has in situ CH4 analyzers at Cape Ochi-ishi (1995-2014) and Hateruma Island (1996-2014) (Tohjima et al., 2002). The Chinese Academy of Meteorological Sciences has measurements at Mt. Waliguan (1994-2014) (Zhou et al., 2004). New measurements in India have been reported by Ganesan et al. (2013). In the Southern Hemisphere, there are long time series of continuous CH4 measurements at Cape Point South Africa (Brunke et al., 1990; Scheel et al., 1990) and Cape Grim Observatory, Tasmania, Australia (Fraser et al., 1986). CH4 is also measured at sites with regional focus. Sasakawa et al. (2010) reported measurements of CH4 from 9 sites in the Japan-Russia Siberian Tall Tower Inland Observation Network started in 2004. Measurements are made from multiple levels on each of the towers; sampling heights vary by tower with a maximum above ground height of 80 m. Kozlova et al. (2008) report measurements of CH4 from 5 levels between 4 and 300 m above ground at a tower in Zotino, Russia. Measurements started in 2007 in China at Lin’an and Longfengshan (Fang et al., 2013).

**CH4 measurements from aircraft:**

*Light aircraft:*

CSIRO Marine and Atmospheric Research (CMAR) collected vertical profiles of discrete air samples 35 km west and upwind of Cape Grim Observatory (39°08’S, 145°14’E) from 1989-2000 (Langenfelds et al., 1996; Francey et al., 1999). Sampling frequency was about monthly for most of the period. Typically, profiles show decreasing CH4 mole fractions up to the boundary layer, then a positive gradient with greater CH4 mole fractions above the boundary layer to 8 km. This is in contrast to profiles in the Northern Hemisphere, which typically have strong negative gradients. CMAR vertical profiles are particularly useful for constraining CH4 and other trace gas emissions from biomass burning in southern Africa and South America (Pak et al., 1996; 1999). NOAA ESRL has had a program to measure CH4 and other LLGHGs from light aircraft since 1992. The program is predominantly focused on N. America and contributes to the North American Carbon program. Air samples are collected with a two-component automated sampling system from ~500 m agl up to ~8 km asl. All samples are analyzed on the same analytical system as other NOAA discrete air samples.

*Commercial and military aircraft:*

Passenger aircraft are a useful sampling platform for systematic CH4 measurements in the upper-troposphere and lower-stratosphere. Typically, discrete air samples are collected in flasks, then analyzed at a central laboratory. CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) and CONTRAIL (Comprehensive Observation Network for Trace Gases by Airliner) have provided invaluable data on atmospheric CH4, particularly in the tropics, where vertical mixing is rapid. CARIBIC is based on a modified air freight container (Brenninkmeijer et al., 2007), which is loaded onto Lufthansa A340 passenger aircraft about monthly and remains on board for 2-4 successive flights. Details of the air sampling and CH4 analysis system for are in Schuck et al. (2009). Each series of flights yields 116 air samples. CONTRAIL uses automated air sampling equipment on 2 JAL Boeing 747 aircraft to collect 12 discrete air samples in titanium flasks on flights returning to Japan (to minimize sample storage times) (Machida et al., 2008; Matsueda and Inoue, 1996). Samples are collected about twice per month. Japan Meteorological Agency, in collaboration with the Meteorological Research Institute, have sampled about monthly since 2011 from a Japan Ministry of Defense C-130H cargo aircraft flying from near Tokyo to Minamitorishima, MNM, (Tsuboi et al., 2013). Twenty four samples are collected manually on the south-bound leg to MNM, 20 at level flight of 6 km and 4 during the decent to the island. These data help fill a gap in the free troposphere over the Western Pacific Ocean, but at lower altitudes than CONTRAIL, which will help constrain Asian sources of CH4. Niwa et al. (2014) reported elevated CH4 for December to March and July to September in samples from 2010 to 2012; concurrent enhancements in and CO in the same samples indicate combustions sources in China as the source of CH4. The ratio, CH4/CO, was greater in summer (1.2 ppb/ppb) than winter (0.47 ppb/ppb) because of additional influence by biogenic emissions. Another extensive CH4 data set from over Japan is based on measurements of discrete air samples collected on flights out of Sendai, Japan. Umezawa et al. (2014) analyze approximately monthly samples from light aircraft up to 4 km asl east of Sendai, Japan and from commercial aircraft between Sendai and Fukuoka, Japan at 4 to 11 km asl from early 1988 to mid-2010. This high-quality data set is useful and long enough to constrain emissions of CH4 from East Asia and how they are changing with time.

*Research aircraft:*

Many aircraft campaigns have been designed to improve understanding of tropospheric chemistry and the processes that produce short-lived species such as O3 (e.g., campaigns under NASA’s Global Tropospheric Experiment). Although CH4 was measured in some of these campaigns, they are too limited in duration to be helpful in understand the budget of atmospheric CH4 and for inclusion in this review. An exception is HIPPO (HIAPER Pole-to-Pole Observations) (Wofsy et al., 2011), a series of 5 north-to-south transects from the Arctic to the Antarctic, each about 4 weeks long. Methane measurements were made with continuous analyzers on board and from discrete samples collected with semi-automated samplers. Each transect also incudes numerous vertical profiles from 1000 ft to 45,000 ft to capture variations in CH4 (and many other parameters) as a function of altitude and latitude. A key finding from HIPPO was elevated values of CH4 over the Arctic Ocean. Kort et al. (2012) used observed enhancements near the surface to calculate emissions of CH4 of 2 mg m-2 d-1 in the region, but the extent of the emissions was unclear.

**Shipboard measurements:**

Commercial, military, and research ships offer a platform to obtain surface measurements of CH4 away from source regions. Most reported measurements are in the Pacific Ocean. Japan Meteorological Agency has measurements of atmospheric CH4 (and CH4 at 5 m depth in seawater) from a quasi-continuous analyzer from the R/V Ryofu Maru available from 1990 to 2013, but at 10 ppb resolution. These data are available from the WDCGG. Terao et al. (2011) analyze CH4 measurements from the two Pacific sampling tracks, one in the western Pacific between Japan and New Zealand at a frequency of 10 transects per year, and one between Japan and N. America at about 6 transects per year. NOAA has shipboard CH4 data from many short periods available at the WDCGG, and multi-year time series from the Pacific Ocean and South China Sea (Dlugokencky et al., 1994), although neither sampling track is active in 2014.

Figure Captions:

Figure 1. Globally averaged CH4 dry air mole fraction at earth’s surface (blue symbols) and deseasonalized trend (red line) (a) and instantaneous growth rate (b). Global means are from NOAA; UCI and AGAGE global means agree well, especially since the early-1990s as shown in Hartman et al. (2013).

Figure 2. Annual total global CH4 emissions (symbols) as a function of time calculated from atmospheric observations using mass-balance and a constant lifetime of 9.1 yr. Dashed lines show average emissions over 1984-2006 and 2007-2013.

Figure 3. Average differences (±1 s.d.) in annual mean CH4 between each NOAA air sampling site and South Pole. Red symbols are fixed surface sites; blue symbols are for Pacific Ocean latitude bins; and green symbols are for South China Sea latitude bins. These patterns are used by CTM studies to infer emissions.