**Introduction to modern measurements of LLGHGs:**

The high-quality observations used to calculate global annual means of long-lived greenhouse gases (LLGHG) in this section are from quasi-continuous analyzers measuring in real time or discrete air samples collected in sample canisters analyzer after collection (typically days to more than a year later). Periods prior to these modern measurements were determined from archived air samples and air extracted from polar ice cores and firn.

All high-quality LLGHG observations, regardless of source, are measured on analyzers calibrated with standards traceable to the SI or derived using primary methods traceable to SI quantities (e.g., temperature, pressure, and mass; SI ≡ International System of units). The quantity measured is technically called “amount of substance fraction” and reported in units of mole fraction, dry air (µmol mol‑1 = ppm; nmol mol‑1 = ppb; pmol mol‑1 = ppt). Mole fraction, unlike concentration, is conserved, i.e., it is unaffected by changes in temperature and pressure as air masses are transported. Use of SI-traceable standards allows reasonable estimates of measurement uncertainties across time scales. Since spatial and temporal patterns in atmospheric observations of LLGHGs are exploited with atmospheric transport models to estimate emissions and losses, measurement uncertainties are crucial in determining uncertainties on GHG budgets.

For most of the discussion in this section and for calculation of RF, global averages are used. Estimates of their uncertainties are more complicated than for the measurements themselves. None of the programs contributing data to this assessment have global coverage, so the global average can only be approximated. Because most observations are at the surface, it is the surface global average (mean) that is reported. The spatial representativeness of the observations must also be consistent with the large scales normally considered to ensure they are weighted properly. Global means presented in AR6 are determined from measurements representative of large well-mixed volumes of the lower troposphere. Measurements showing evidence of local pollution, or from sites directly influenced by local and regional pollution, are excluded. Global averages that include pollution events or sites subject to more regional or local influence will tend to show higher mole fractions (Table 2.X).

**Carbon Dioxide (CO2):**

Globally averaged CO2 (or its proxy) calculated by smoothing direct measurements starting in 1958 is plotted in figure 2.xa. Dominating the signal is a long-term trend driven by emissions of CO2 from fossil fuel combustion and cement production. Based on observations and inventories of fossil fuel CO2 emissions, Ballantyne et al. (2012) showed that the increasing atmospheric burden accounts for 54% of these emissions. Observations of atmospheric CO2 abundance and O2/N2 (Manning and Keeling, 2006) and measured increases in ocean carbon (Sabine et al., 2004) indicate that most of fossil fuel CO2 emissions were taken up by the ocean (Tans, 2009), where they also impact the marine food chain by making the oceans more acidic. While the terrestrial biosphere is currently a net sink for CO2, historically, emissions from land-use change (e.g., deforestation) about balance uptake (e.g., Tans, 2009). Since AR5 (2011), globally averaged annual mean CO2 increased by 14.54 ± 0.15 ppm to 404.98 ± 0.13 ppm in 2017. From 2011-2017, the average annual increase was 2.38 ppm with a standard deviation of 0.42 ppm. CO2’s instantaneous growth rate, calculated as the time-derivative of the deseasonalized trend (Fig. 2.xb), shows more clearly that the rate of increase varies significantly, e.g., very large growth during the El Niño of 2015-2016 (Betts et al., 2016; Bastos et al., 2013). Measurements of δ13C(CO2) indicate that variability is caused by relatively small variations in large two-way fluxes between the atmosphere and terrestrial biosphere (photosynthesis and respiration; see Chapter X) rather than the ocean sink. Observations provide other constraints on the CO2 budget, including spatial gradients and seasonal cycles, and how they change over time. These aspects of the data are explored further in Chapter X.

**Methane (CH4):**

Globally averaged CH4 at Earth’s surface in 2017 was 1849.6 ± 1.1 ppb, an increase of 46.4 ± 1.2 ppb since AR5 (2011). Figure 2.ya shows reasonably good agreement among multiple labs producing global means. The atmospheric CH4 time series results from a complex mix of sources and sinks, with emissions from both anthropogenic (~60%) and natural (~40%) sources. Oxidation of atmospheric CH4, initiated by reaction with short-lived hydroxyl radical (OH), is the main loss and largest term in the atmospheric CH4 bud­get of sources and sinks. Over the period of direct observations, atmospheric CH4 shows interesting changes. From the late-1970s through the early-2000s, CH4’s growth rate was decreasing, and its atmospheric burden was approximate constant from 1999-2006. Assuming constant atmospheric CH4 lifetime, this behavior is consistent with constant total global emissions (Dlugokencky et al., 2011), but the magnitude and trend in emissions from individual sources and trends in CH4 atmo­spheric lifetime are still highly uncertain. In 2007, CH4 began increasing again. Observations are insufficient to identify with certainty changes to CH4’s complex budget, but measurements of δ13C(CH4) indicate a strong influence of microbial sources (Nisbet et al., 2016; Nisbet et al., 2019; Schaefer et al., 2016), rather than fossil fuel sources (Schwietzke et al., 2016). Changes to emissions from other CH4 sources (e.g., Worden et al., 2017; Thompson et al., 2019) and CH4 loss rate (Prather and Holmes, 2017; Naus et al., 2019) have also been implicated, but remain uncertain.

**Nitrous Oxide (N2O):**

AR5 reported 324.2 ± 0.1 ppb for global annual mean N2O in 2011; since then, it increased by 5.1 ± 0.2 ppb to 329.4 ± 0.2 ppb in 2017. Globally averaged N2O is plotted in Figure 2.za with its instantaneous growth rate in Figure 2.zb. From 2008-2017, the N2O global mean annual increase averaged 0.9 ppb with a standard deviation of 0.2 ppb, and it is increasing.

The PI atmospheric burden of N2O was a balance between natural emissions and loss processes (photolysis and reaction with O(1D)) in the stratosphere. About 6% of the loss creates NO, which destroys stratospheric ozone. Agriculture, particularly use of nitrogen-containing fertilizers and manure, is the largest anthropogenic source (Park et al., 2012). Atmospheric N2O global annual averages combined with an estimate of its lifetime (123 yr, with most likely range 104-152 yr (SPARC, 2013)), show its budget of emissions and sinks is out of balance by ~40%.

N2O is interesting from a measurement perspective. Its observed background spatial gradients are quite small (e.g., ~1.7 ppb between the northern subtropics and high southern latitudes), so excellent precision and internal consistency are extremely important. WMO’s Global Atmosphere Watch (GAW) program recommends inter-network compatibility of 0.1 ppb (WMO, 2018). Achieving this scientific goal is difficult with historically-used methods (gas chromatography with electron capture detection), and rarely achieved among GAW participants. While measurement quality is sufficient to quantify the atmospheric N2O budget at large spatial scales, determining emissions at policy relevant scales is more challenging.

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**Figure Captions:**

Figure 2.x: (a) Globally averaged CO2 dry-air mole fractions from Scripps Institution of Oceanography (SIO) at annual time resolution based on measurements from Mauna Loa, Hawaii and South Pole (red), CSIRO at monthly time resolution (cyan), and NOAA/ESRL/GMD at quasi-weekly time resolution (blue). SIO values are deseasonalized. (b) Instantaneous growth rates for globally averaged atmospheric CO2 using the same color code as in (a). Growth rates are calculated as the time derivative of the deseasonalized global averages (Dlugokencky et al., 1994).

Figure 2.y: (a) Globally averaged CH4 dry-air mole fractions from UCI (green; four values per year, except prior to 1984, when they are of lower and varying frequency), AGAGE (red; monthly), CSIRO (cyan; monthly), and NOAA/ESRL/GMD (blue; quasi-weekly). (b) Instantaneous growth rate for globally averaged atmospheric CH4 using the same colour code as in (a). Growth rates were calculated as in Figure 2.x.

Figure 2.z: (a) Globally averaged N2O dry-air mole fractions from AGAGE (red), CSIRO (cyan), and NOAA/ESRL/GMD (blue) at monthly resolution. (b) Instantaneous growth rates for globally averaged atmospheric N2O. Growth rates, calculated as in Figure 2.x, were begun in 1995; prior to that, data were too noisy to calculate reliable instantaneous growth rates.