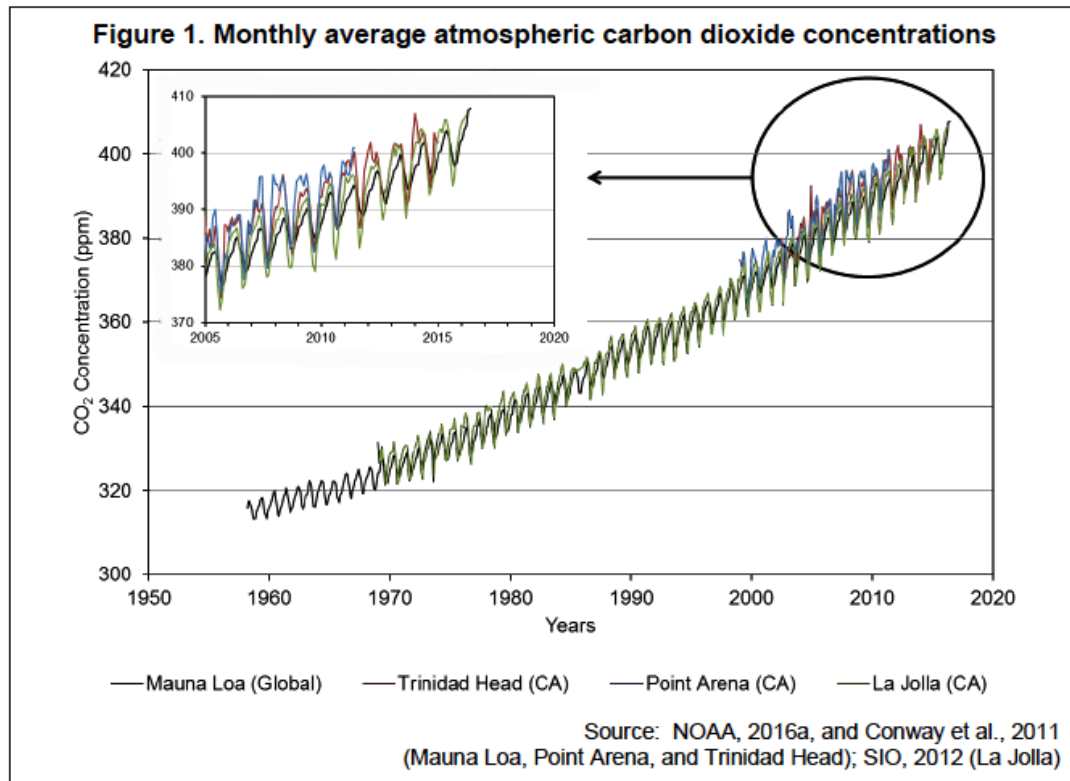


ATMOSPHERIC GREENHOUSE GAS CONCENTRATIONS

Atmospheric concentrations of greenhouse gases such as carbon dioxide, methane, nitrous oxide and certain fluorinated gases continue to increase globally and in California. In 2015, the annual average global concentrations of carbon dioxide exceeded 400 parts per million. Levels are expected to remain above this benchmark for many generations.



What does the indicator show?

Atmospheric concentrations of greenhouse gases are increasing, as illustrated in Figures 1-4. These graphs show the ambient concentrations of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and a variety of fluorinated gases (F-gases) at a global background site at the peak of Mauna Loa on the island of Hawaii, and for CO₂ and CH₄, at three regional background sites in California. The measurements are presented in parts per million (ppm) or parts per billion (ppb). These are units of air pollution mixing ratios commonly used to describe ambient air pollution concentrations (1 ppm = 1,000 ppb).

Figure 1 shows the CO₂ measurements at Mauna Loa, and at three coastal sites in California (Trinidad Head, Point Arena, and La Jolla). Measurements at Mauna Loa first began in 1958. Since then, in under six decades, CO₂ concentrations have increased from 315 ppm to over 400 ppm, and continue to trend upward. In general, in the last five years, the annual average CO₂ concentrations have increased by 2 ppm or more per year (NOAA, 2017). The measurements in California have slightly higher values and



larger variabilities compared to those at Mauna Loa, primarily due to influences from anthropogenic CO₂ emission sources near the regional monitoring sites.

Figure 2 shows the atmospheric measurements of CH₄ at Mauna Loa since 1983. The figure also shows the CH₄ measurements at Point Arena and Trinidad Head since 1999 and 2002, respectively. Global CH₄ levels have increased since 1983, except for a brief period between 1999 and 2006 when they were relatively constant before increasing again in 2007. Pre-industrial (i.e., pre-1750) CH₄ concentrations were approximately 0.7 ppm. By contrast, today's atmospheric CH₄ concentrations exceed 1.8 ppm at Mauna Loa and the California sites – an increase of over 150 percent (WMO, 2016). However, the CH₄ concentrations at the California sites are higher than those observed at Mauna Loa. This is likely due to a strong latitudinal gradient that promotes elevated CH₄ concentrations in the northern latitudes, where there are more human activities that lead to greater emissions (Frankenberg et al., 2005).

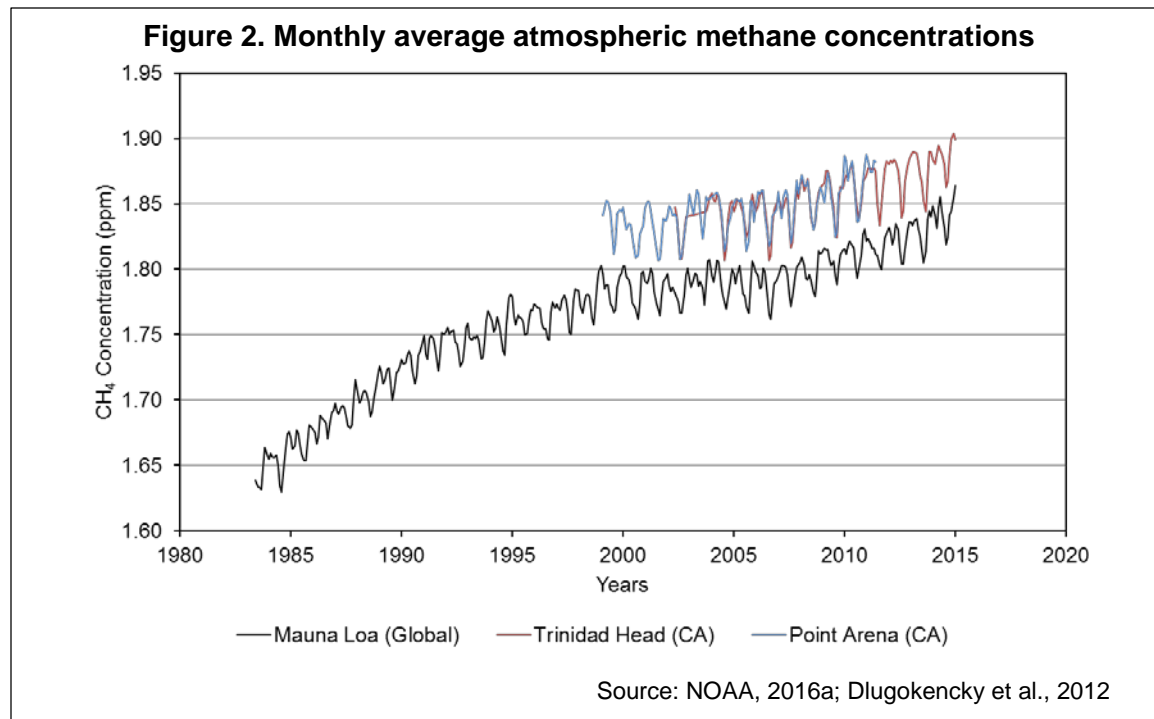


Figure 3 shows the atmospheric concentrations of N₂O at Mauna Loa since 1987. N₂O concentrations have been increasing globally at a rate of approximately 0.7 ppb per year over the past few decades (IPCC, 2014). Global N₂O levels in 2016 were approximately 22 percent greater than pre-industrial levels of 270 ppb (WMO, 2016).



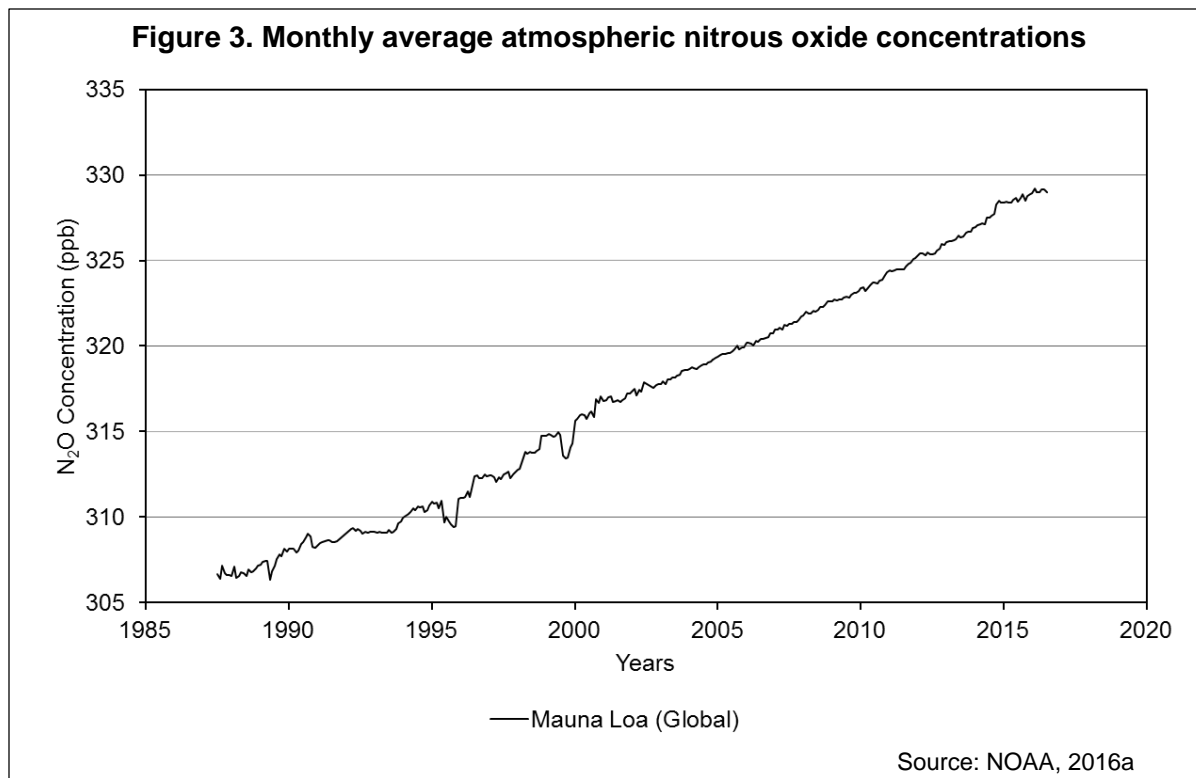
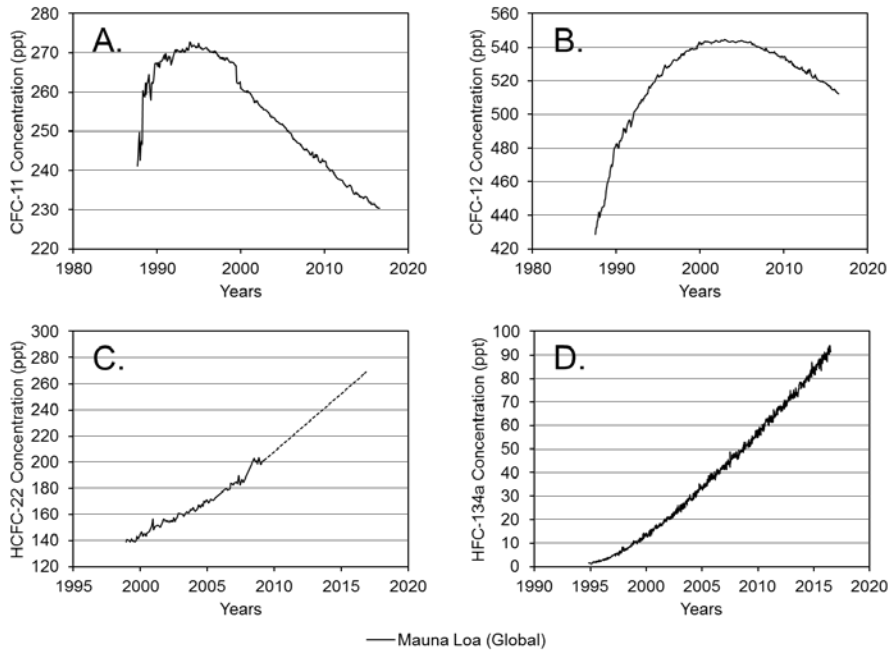


Figure 4 shows the atmospheric concentrations of select chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) which are the most prevalent F-gases in the atmosphere at Mauna Loa, specifically trichlorofluoromethane (CFC-11) (panel A), dichlorodifluoromethane (CFC-12) (panel B), chlorodifluoromethane (HCFC-22) (panel C), and 1,1,1,2-tetrafluoroethane (HFC-134a) (panel D). CFCs and HCFCs are synthetic compounds that began to appear in the atmosphere in the 20th century as a result of their increased usage as refrigerants. The pre-industrial CFC and HCFC concentrations are assumed to be zero. Hydrofluorocarbons (HFCs) are primarily used as substitutes for CFCs and HCFCs following the phase out and ban on these ozone-depleting substances pursuant to the Montreal Protocol of 1987.

Since they were first measured at Mauna Loa in 1987, concentrations of CFC-11 and CFC-12 have rapidly increased. Following their production ban in 1996, atmospheric CFC concentrations at Mauna Loa began to decrease steadily (UNEP, 2012). Atmospheric concentrations of HCFC-22 increased at Mauna Loa between the late 1990s, when they were first measured, and 2009; no data are available from 2009 to 2015. Atmospheric concentrations of HFC-134a have also been increasing globally over the past two decades at a steady rate of approximately 5 ppb per year since 2005. Its global background concentrations have increased by over 68 times since its first record at Mauna Loa in 1994, and now exceed 200 ppb.



Figure 4. Monthly average atmospheric F-gas concentrations

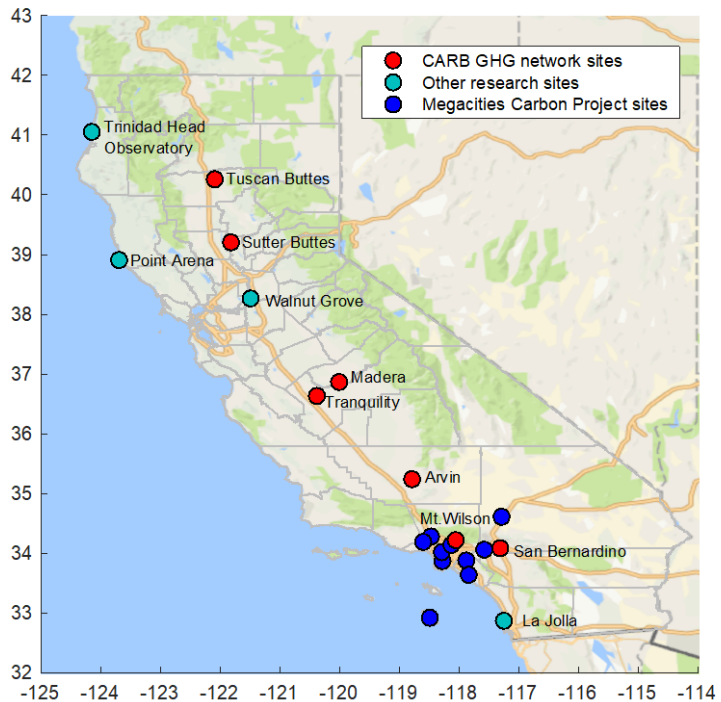


Note: HCFC-22 measurements were not available from 2009-2015, and have been marked with a dashed line on Panel C.

Source: NOAA, 2016a

California has undertaken additional efforts to track the changes in ambient GHG concentrations at several monitoring sites located throughout the state. As shown on the map in Figure 5, the California Air Resources Board (CARB) operates or funds eight GHG monitoring network sites in the state. The map inset also shows 13 additional monitoring sites that are operating under various research partnerships and collaborations (most notably the Megacities Carbon Project in Los Angeles (NASA-JPL, 2017)). These sites study the regional and local emission sources of important GHGs in California.

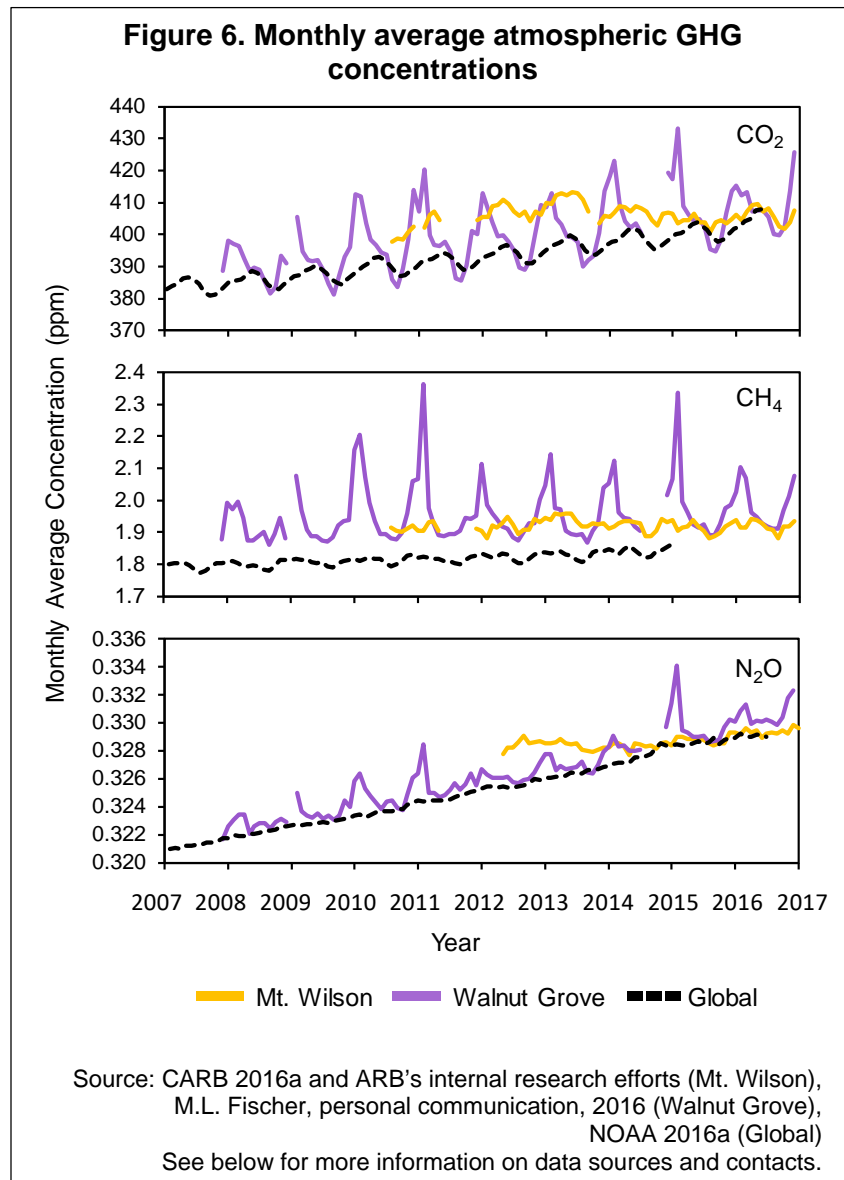
Figure 5. Greenhouse gas monitoring locations in California



Source: CARB, 2016



Aside from the three coastal background sites (NOAA, 2016a), California's GHG monitoring network also employs two stations that measure well-mixed regional air, which can be used to understand how GHG concentrations are changing in California relative to the global trends. The Mt. Wilson station, located on top of the San Gabriel Mountains in Los Angeles County, offers a good indication of air quality in Southern California, as it receives well-mixed air parcels from the Los Angeles air basin every day. The Walnut Grove station, an inland tower located near Sacramento, provides a signature of regional emissions from Northern and Central California.



CO₂ concentrations at inland locations in California track the global trends well, albeit with larger inter-annual variabilities and higher monthly average concentrations (Figure 6). The average CO₂ concentration at Mt. Wilson increased from roughly 400 ppm in 2010 to over 410 ppm by 2013, which translated to an enhancement of approximately 3 ppm per year. Since 2013, CO₂ concentrations at Mt. Wilson have not shown any significant annual variation. By comparison, the Walnut Grove tower experienced CO₂ enhancement of approximately 2 ppm per year. However, inter-annual variabilities were considerably larger with the monthly average concentrations at Walnut Grove reaching a maximum of over 420 ppm. The more

pronounced seasonal pattern at the Walnut Grove site can be attributed to influence from local sources as well as lower average mixing depths, which trap air pollution emissions closer to the ground during cooler months.



CH₄ concentrations in California also show higher values and larger variabilities relative to the global trend. At Mount Wilson, the monthly average CH₄ enhancement above the global background is typically within a fraction of a ppm. However, it continues to track the general trend of the global background measured at Mauna Loa. During summer months, CH₄ measurements at Walnut Grove are similar to measurements at Mt. Wilson. Higher concentrations during the winter months are likely due to influences from changing meteorological conditions and human activities. These measurements show that the general CH₄ concentration has remained relatively stable over the past decade.

Except for the years prior to 2015, N₂O concentrations at Mt. Wilson were similar to those at Mauna Loa. By contrast, the trend in N₂O concentrations at Walnut Grove closely mirrored the global trend, with summer time N₂O concentrations that were similar to global background concentrations. N₂O production rates change throughout the year based on parameters like soil moisture content, meteorology, and microbial activities, which may be contributing to the variability in N₂O concentrations observed at Walnut Grove. Furthermore, N₂O concentrations at Walnut Grove have been increasing by approximately 1 ppb per year, similar to the global trend.

Why is this indicator important?

Global temperatures are directly linked to GHG levels in the atmosphere (IPCC, 2013). The 2015 Paris Agreement aims to hold the increase in the global average temperature to well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature increase even further to 1.5°C above pre-industrial levels (UNFCCC, 2016). Emissions scenarios leading to CO₂-equivalent concentrations of about 450 ppm or lower in 2100 are likely to maintain warming below 2°C over the 21st century relative to pre-industrial levels (IPCC, 2014). Some climate scientists argue that a reduction from the current level of CO₂ in the atmosphere to 350 ppm CO₂ by 2100 will be essential to avoid dangerous anthropogenic climate change (Hansen et al., 2013). Thus, ambient concentration trends are an important indicator for changes in GHG emissions and their accumulation in the atmosphere. In particular, CO₂, CH₄, N₂O, F-gases, and black carbon (discussed in the *Atmospheric black carbon concentrations* indicator) are considered to be the most important anthropogenic drivers of climate change.

CO₂ is a long-lived GHG responsible for roughly 65 percent of the total warming effect caused by GHGs globally. It contributes to over 84 percent of the current GHG emission inventory in California on a 100-year timescale (CARB, 2016a; WMO, 2016). Since CO₂ is typically well-mixed in the atmosphere, measurements at remote sites can provide integrated global background levels. The first and the longest continuous measurements of global atmospheric CO₂ levels were initiated by Charles D. Keeling in 1958 at Mauna Loa. For the first time, these measurements documented that atmospheric CO₂ levels were increasing globally. In the 1980s and the 1990s, it was recognized that greater coverage of CO₂ measurements was required to provide the basis for estimating the emission impacts of sources and sinks of atmospheric CO₂ over land as well as ocean regions. Since CO₂ remains in the atmosphere for many



centuries, its atmospheric levels can continue to increase even if its emissions are significantly reduced.

Atmospheric CH₄, N₂O, and F-gases contribute roughly 17 percent, 6 percent, and 12 percent respectively of the radiative forcing caused by globally well-mixed GHGs (IPCC, 2013; WMO, 2016). These pollutants could play an even more important role owing to their greater 100-year global warming potentials (100-year GWP) as compared to that of CO₂ (GWP = 1). Some of these GHGs have a much shorter life than that of CO₂. These can cause significant climate impact in the near term, and are considered short-lived climate pollutants (SLCPs). For instance, CH₄ has a 100-year GWP of 28, and remains in the atmosphere for about 12 years before removal, whereas F-gases such as HCFC-22 and HFC-134a have GWPs of over a thousand, and can remain in the atmosphere for one to two decades. On the other hand, N₂O has a GWP of 265 and remains in the atmosphere for roughly 120 years, which can result in long-term climate impacts (IPCC, 2014).

High-precision measurements, such as those presented in this indicator report, are essential to understanding GHG emissions from various sources – including human activities, atmospheric processes, plants, soils, and oceans. Tracking the life cycles of these GHGs provides information necessary for formulating mitigation strategies. Data on atmospheric GHG levels, in particular, are needed to project future climate change associated with various emission scenarios, and to establish and revise emission reduction targets (IPCC, 2013).

In California, regional GHG emission sources contribute to enhancements in the concentrations of CO₂, CH₄, and N₂O above global background levels. In addition to the monitoring and measurement efforts undertaken by various research teams, CARB has also funded several studies to utilize the atmospheric measurements from regional GHG monitoring sites to infer the most likely distribution and strength of regional CO₂, CH₄, and N₂O emission sources in California (Fischer and Jeong, 2016; Zhao et al., 2009).

What factors influence this indicator?

The concentrations of CO₂, CH₄, N₂O, and F-gases in the atmosphere reflect the difference between their rates of emission and their rates of removal. The majority of the changes observed in the global and regional GHG trends are directly related to human activities such as fossil fuel combustion, biomass burning, industrial processes, agricultural practices, and deforestation (IPCC, 2013). Additional discussion of factors affecting the emission of these GHGs in California is presented in the *Greenhouse gas emissions* indicator.

CO₂ is continuously exchanged between the land, the atmosphere, and the ocean through physical, chemical, and biological processes (IPCC, 2013). Prior to 1750, the global background CO₂ concentration was estimated to be less than 280 ppm (WMO, 2016). During this period, the amount of CO₂ released by natural processes (e.g., respiration and decomposition) was almost exactly in balance with the amount absorbed



by plants during photosynthesis and other removal processes (Tans and Keeling, 2012; WMO, 2016). The increase in the CO₂ concentration today derives primarily from emissions related to fossil fuel combustion and biomass burning. It is also directly related to changes in agricultural practices and deforestation (IPCC, 2013). While more than half of emitted CO₂ is removed through natural processes within a century, about 20 percent remains in the atmosphere for many millennia (Archer et al., 2009). Consequently, atmospheric CO₂ will continue to increase in the atmosphere even if annual CO₂ emissions are substantially reduced from present levels. It should be noted that, while increasing levels of atmospheric CO₂ are affecting climate, changes in climate are likewise affecting the processes that lead to CO₂ uptake from, and release into, the atmosphere (IPCC, 2013).

Atmospheric CO₂ concentrations reflect regional, as well as seasonal and inter-annual influences. Due to its higher fossil fuel emissions, the Northern Hemisphere has higher CO₂ concentrations than the Southern Hemisphere. Seasonal variations are attributed to seasonal patterns of plant growth and decay. Inter-annual variations have been attributed to El Niño and La Niña climate conditions; generally, higher-than-average increases in CO₂ correspond to El Niño conditions, and lower-than-average increases correspond to La Niña conditions (IPCC, 2013).

Atmospheric CH₄ originates from both natural and anthropogenic sources. CH₄ is emitted from wetlands, oceans, termites, and geological sources. Anthropogenic sources of methane include rice agriculture, livestock, landfills, waste treatment, biomass burning, and fossil fuel and natural gas exploitation (i.e., extraction, transmission, distribution, and use). The production of CH₄ by many of these sources is influenced by anaerobic fermentation processes and climate variables (notably temperature and moisture). Atmospheric removal of CH₄, on the other hand, is driven by oxidation processes, a process likewise affected by climate variables.

Atmospheric N₂O is naturally present in the atmosphere as part of the Earth's nitrogen cycle. Its primary driver is the breakdown of nitrogen by microorganisms that live in soil and water (Anderson et al., 2010). Human activities such as agriculture, fossil fuel combustion, wastewater management, and industrial processes account for 40 percent of total N₂O emissions globally (US EPA, 2016). In California, N₂O is emitted in large part from agricultural activities such as soil and manure management. In 2014, these contributed to roughly 65 percent of total statewide N₂O emissions (CARB, 2016a). Most of the remaining 35 percent were attributed to the transportation, industrial, commercial, and residential sectors. Commercial and residential application of synthetic fertilizers over soil and lawn, in particular, plays a significant role in the nitrogen cycle; the release of N₂O from such fertilizers has been shown to exhibit seasonal variability based on their rate of application and watering events.

N₂O from fossil fuel combustion can vary significantly based on the technology, maintenance, and operation of combustion equipment (Graham et al., 2009; Huai et al., 2004). N₂O is prevalent in the tail-pipe exhaust of motor vehicles when their engines and catalytic converters are operating at sub-optimal conditions. N₂O is also typically



generated as a by-product of synthetic fertilizer and other synthetic nitrogen production processes. On the other hand, N₂O is removed from the atmosphere through bacterial activities and through photochemical reactions (US EPA, 2016).

F-gases do not exist in the natural environment; they are only emitted from anthropogenic sources and are only removed through photochemical reactions in the upper atmosphere. F-gases have been used primarily as refrigerants in a variety of applications, including stationary refrigeration and air conditioning, industrial production and manufacturing processes, the transmission and distribution of electricity, and vehicle air conditioning systems. CFC-11, CFC-12, HCFC-22, and HFC-134a emissions derive largely from fugitive leaks, venting during the maintenance and servicing of equipment, leaks from improperly maintained or damaged equipment, and the improper disposal of equipment (Gallagher et al., 2014). International, national, and state regulations affect the use, emission, and eventual atmospheric concentrations of these substances. As noted above, pursuant to the Montreal Protocol of 1987, CFCs were phased out and banned in the United States in 1996; HCFCs will be phased out of new production and consumption by January 1, 2020. Driven by the phase-out of these ozone-depleting substances and by increased demand for refrigeration and air conditioning, HFCs became the fastest growing sources of GHG emissions in California and globally. They are now subject to a production and consumption phasedown under the Kigali Amendment (to the Montreal Protocol) starting in 2019 in ratified developed countries. The first group of developing countries ratified in the amendment will begin the phasedown in 2029. The second group of developing countries will have until 2032 to begin a phasedown. It is important to note that the Kigali Amendment has yet to be ratified by the United States. In addition, California's Senate Bill 1383 (Statutes of 2016) requires statewide reduction of HFC emissions to 40 percent below 2013 levels by 2030 (CARB, 2017). California is moving forward in adopting high global warming HFC prohibitions in certain stationary refrigeration and foam end uses that were originally subject to the US EPA Significant New Alternatives Policy program (SNAP) which was recently vacated by a court case. A legislative bill, Senate Bill 1013 (introduced in February 2018) proposes to adopt the federal SNAP program in its entirety and includes a provision for an incentive program to increase the adoption of low global warming refrigerant technologies. In addition to national and international measures, California has identified additional HFC reduction measures that will be needed to meet the SB 1383 target.

Technical Considerations

Data Characteristics

The CO₂ data presented above are a combination of data from the Scripps Institution of Oceanography (SIO), the National Oceanic and Atmospheric Administration's Earth System Research Laboratory (NOAA-ESRL), Lawrence Berkeley National Laboratory (LBNL), and CARB. In particular, NOAA-ESRL leads the Carbon Cycle Cooperative Global Air Sampling Network, an international effort which utilizes regular discrete samples from baseline observatories, cooperative fixed sites, and commercial ships (NOAA, 2016b). Air samples are collected weekly in glass flasks and CO₂ is measured by a non-dispersive infrared absorption technique (Keeling et al., 2001). The



measurements at Mauna Loa were initiated by C. David Keeling of SIO, and date back to March 1958 (Conway et al., 2007). Monitoring at Point Arena started in January 1999, and at Trinidad Head in April 2002. At the SIO La Jolla Pier, roughly one sample is collected each month during the period of record.

CARB initiated continuous GHG measurements at Mt. Wilson in 2010 (with pilot measurements in 2007) in efforts to improve spatial and temporal understanding of emission sources and regional GHG enhancements throughout California. Mt. Wilson is the longest running CARB site that employs real-time high-precision cavity ring-down spectroscopy (CRDS), and collects continuous CO₂ data every second. Mt. Wilson measures well-mixed urban emissions from the Los Angeles air basin at mid-day, when the atmospheric boundary layer height grows due to surface heating. The atmospheric boundary layer is the lowest part of the atmosphere that is most influenced by air pollution emissions from human activities. It also measures the well-mixed background concentration above the boundary layer during nighttime conditions.

Data collection at Walnut Grove tower began in 2007 through collaboration between researchers at LBNL and NOAA, with support from NOAA, the U.S. Department of Energy (DOE), California Energy Commission (CEC), and CARB. The site was equipped with an automated flask sampling system and real-time analyzers. These provide measurements of a suite of GHGs as well as other compounds including the radiocarbon of CO₂. The Walnut Grove site is the first tall tower site in the world with continuous CH₄ measurements (under NOAA-ESRL's Global monitoring Division).

CH₄ data presented in this report were obtained from the NOAA-ESRL, LBNL, and CARB networks. NOAA-ESRL collected ambient air samples in evacuated flasks to detect CH₄ using a flame ionization detector (FID) integrated with a gas chromatograph (GC) system. CARB conducts continuous air measurements of CH₄ using CRDS (as described previously) with the same collection frequency and quality control protocols. CH₄ monitoring at Mauna Loa began in 1983, Point Arena in 1999, Trinidad Head in 2002, and Mt. Wilson in 2010.

N₂O data presented in this report were obtained from the NOAA-ESRL, LBNL, and CARB. NOAA-ESRL collected ambient air samples in evacuated flasks and utilized *in situ* systems to measure N₂O. CARB and LBNL use off-axis integrated cavity output spectroscopy to continuously measure N₂O at Mt. Wilson and Walnut Grove, respectively. Quality control protocols similar to those applied for CH₄ and CO₂ measurements are instituted to obtain high-precision measurements.

F-gas data presented in this report were obtained from the NOAA-ESRL network. NOAA-ESRL utilizes evacuated flasks to collect ambient air at Mauna Loa and analyzes samples using GC systems integrated with an electron-capture detector (ECD) and a mass spectrometer (MS).



Strengths and Limitations of the Data

Measurement data from NOAA-ESRL undergoes critical evaluation for quality control (NOAA, 2016c). The long-term record at La Jolla, particularly when compared with the longer-term data at Mauna Loa, presents valuable time-series information for tracking CO₂ trends over the past half century (SIO, 2012). These data are useful for characterizing seasonal variations and provide information about the coastal air that travels into California. Although the La Jolla Pier at SIO extends considerably into the ocean, the site can receive some air currents polluted with urban CO₂ emissions from the Los Angeles area that mix with the oceanic and San Diego atmosphere. Likewise, the Point Arena monitors, although coastal, occasionally capture on-shore CO₂ emissions. The Trinidad Head monitor sits on a peninsula extending into the ocean with a tower, however, the air coming from the Pacific Ocean can back up on the nearby coastal range mountains and backflow to the site, thus impacting the measurements of CO₂ in the on-shore air.

CARB's Ambient GHG Monitoring Network was established in 2010 to study regional GHG emissions trends throughout California. The data collected from the GHG Monitoring Network is also critical in evaluating regional and statewide inventories in support of California's climate program (CARB, 2016b). These efforts rely heavily on highly accurate and precise measurements of ambient GHGs analyzed using state-of-the-science instruments. The network is comprised of eight monitoring stations located throughout California, and CARB has equipped these stations with highly accurate and precise analyzers used to measure crucial climate influencers such as CO₂, CH₄, N₂O, and black carbon (BC). Data from this network are used in several research studies. They also form the basis of a comprehensive statewide inverse receptor-oriented modeling effort (Fischer and Jeong, 2016), as well as various trend analysis studies used to verify and inform the statewide GHG emission inventory in California.

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