PRIORITY PARAMETERS AND THEIR MEASUREMENTS

Constance M. Brown-Mitic and Roger Bales
University of Arizona, Tucson, Arizona, USA

Samuel K. Kaharabata
Agriculture and Agri-Food, Ottawa, Ontario, Canada

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Summary

This paper outlines some basic atmospheric parameters that are considered of high importance for monitoring. Comprehensive monitoring of atmospheric compounds that adversely affect human health, or significantly impact Earth’s climate and overall ecosystem functioning, is a priority for management and mitigation strategies. A wide range of proven measurement techniques are now available, by which the large uncertainties in the magnitudes of emissions from identified sources can be lowered with longterm and widespread measurement campaigns. This is particularly important when determining the impact of adopted mitigation strategies on the atmospheric budgets. Better knowledge of the sources and sinks also helps modelers develop and improve algorithms that describe exchange processes (e.g., deposition characteristics), and facilitates the interpretation of climate model predictions on the effects of radiative forcing by greenhouse gases. There are basically two types of atmospheric monitoring networks, although they are not mutually exclusive of each other. One measures atmospheric pollutants, and one measures parameters that influence interrelationships and functioning of the Earth-atmosphere system. The priority parameters monitored from both of these networks, the major networks in operation and some techniques used in monitoring are discussed.

1. Introduction
Over the twentieth century, human activities such as the use of fossil fuel, agricultural practices and deforestation have been affecting the climate by altering the composition of Earth’s atmosphere. These activities have resulted in increasing concentrations of many gasses such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), tropospheric ozone (O₃), and aerosols in the atmosphere. These gases have the ability to trap outgoing longwave in the atmosphere resulting in an increase in the atmospheric temperature. This enhanced greenhouse effect has the potential to significantly modify climatic conditions.

The increase in these greenhouse gases over time and their effects on our climate have been documented and discussed considerably in the literature from 1980 to 2000. Good sources for the reader to start with are the publications by the Intergovernmental Panel on Climate Change (IPCC). Due to the growing concern that human activities are changing the atmosphere and climate, several global efforts to reduce greenhouse gas emissions have been made. Recent international meetings highlight these efforts and they include the Montreal Protocol, which although not specifically focused on greenhouse gas emissions at the time, agreed to limit ozone layer depleting chemicals, which are themselves greenhouse gasses, the 1992 Rio de Janeiro Climate Change Convention, and the 1997 Kyoto Protocol where 147 countries signed an agreement to curb emissions.

In addition to the effect for climate warming, the changing composition of Earth’s atmosphere has a direct effect on air pollution and the general health of the global ecosystem for plants and animals alike. There is a need to understand the sources and sinks of the important atmospheric gasses, their interaction with the surface and their chemical and physical transformations. It becomes necessary to monitor atmospheric properties that will help us to understand how the atmosphere works, and the interrelationship with vegetation, soils, and water.

To address these issues, discrete measurements from land and sea surfaces, discrete spatial sampling from aircraft, and continuous observations from towers are been made for an increasing number of different ecosystems. This approach establishes baseline values for significant climatic and ecophysiological parameters. It also documents the temporal and spatial distributions of the important gasses and provide essential constraints to our understanding of atmosphere-Earth system.

Parameters that have been identified as significant for atmospheric monitoring, may be placed into categories according to their impact and how they are used. For the purpose of this article atmospheric parameters for observation may be prioritized into two basic categories. These categories are in no way mutually exclusive as there are gasses that may fall into both categories. The first category is parameters that reflect air quality and are important for pollution and health issues. The second is parameters that reflect ecosystem dynamics and are important for climate and global change issues.

The following sections gives a brief description of the parameters that have a high priority for monitoring, how they are measured and used, and any gaps
which may exist in these areas.

2. Parameters that Reflect Air Quality

Urban air pollution is a significant environmental problem, resulting from human activities that disturb the chemical and optical properties of clean air. There is a standard set of parameters that are used to indicate ambient air quality for the purposes of pollution and public health issues. These are considered to be toxic pollutants, in that they are known to cause serious human health problems. Toxic pollutants are regularly emitted by vehicles and a variety of industries, as well as soils, waste, dumps, and agricultural fields. The pollutants can exist in a gaseous form or as particles. Atmospheric monitoring is essential to track these pollutants, as many are volatile and can travel long distances.

Between 1900 and 1970, there was a significant increase in ambient levels of air pollution in North America. Nitrogen oxides (NO\textsubscript{x}) increased by 690%, volatile organic compounds (VOC) increased by 260%, and sulfur dioxide (SO\textsubscript{2}) increased by 210%. Although in the USA the Clean Air Act was signed into law in 1970, pollution levels continued to rise until its amendment in 1977 at which point air pollution levels started to decrease. Reduction in concentrations have occurred in carbon monoxide (CO) by 37%, lead (Pb) by 78%, nitrogen dioxide (NO\textsubscript{2}) by 14%, ozone (O\textsubscript{3}) by 6%, particulate matter (PM-10) by 22%, sulfur dioxide (SO\textsubscript{2}) by 37%, and in emissions of CO (6%), Pb (32%), NO\textsubscript{2} (3%), VOC (9%), PM-10 (17%), and SO\textsubscript{2} (18%) between 1986 and 1994. Similar reductions have also occurred in Canada as reported by the National Air Pollution Surveillance network (NAPS). Treaties and agreements such as the Long-Range Trans-boundary Air Pollution Agreement in 1988, the Montreal Protocol (indirectly), adopted in 1987 and its amendments in 1990 and 1992, and the Kyoto Protocol in 1997 have had a significant effect in the reduction of air pollutants. Air pollution levels would have continued to rise without these controls, and still require continuous monitoring for management and continued reduction controls. The principal pollutants as identified by national air quality organizations such as the United States' Environmental Protection Agency, Mexico City Direction for Pollution Prevention and Control, and the United Kingdoms' Department of Environment, Transport and Regions, are CO, NO\textsubscript{x}, O\textsubscript{3}, Pb, PM, and sulfur oxides (SO\textsubscript{x}).

2.1. Carbon Monoxide

Carbon monoxide is a result of incomplete combustion of fuels and carbon containing substances such as gasoline and diesel. It combines with hemoglobin to form carboxyhemoglobin that can reach lethal levels. It reduces the ability of blood to carry oxygen, alters the nervous system, causes headaches, fatigue, drowsiness, respiratory failure, and even death. CO has recently been identified as a cause for the increasing concentration of methane, which is a potent greenhouse gas. The US National Ambient Air Quality Standard (NAAQS) for CO has an eight-hour average of 9 parts per million by volume (ppm) and 35 ppm for the one-hour average. The Mexico Automatic Atmospheric Monitoring
Network (RAMA) has a maximum eight hour average of 11 ppm.

2.2. Nitrogen Dioxide

Nitrogen dioxide is an acidic air pollutant resulting from the high temperature combustion processes in vehicles and electrical storms. \( \text{NO}_2 \) causes lung irritation, aggravates cardiovascular and respiratory diseases in humans and premature leaf loss and inhibition of growth in plants. It is also a major precursor pollutant leading to the formation of tropospheric ozone.

Emissions of nitrogen oxides (NO\(_x\)) consist primarily of nitric oxide (NO), which can be oxidized by ozone and/or peroxo radicals to form nitrogen dioxide (NO\(_2\)). During the day, NO\(_2\) reacts with hydroxyl radical to form nitric acid, which is the principal means of nitric acid formation. Conversion rates for NO\(_2\) to nitric acid range from <1 to 90%/hour. The US NAAQS has an annual mean for NO\(_2\) of 0.053 ppm, and Mexico RAMA has a maximum one hour average of 0.21 ppm.

2.3. Sulfur Dioxide

Sulphur dioxide is an acidic pollutant, which oxidizes and combines with water to form sulfuric acid, which is the main component of acid rain in the eastern parts of the United States. The main sources of SO\(_2\) are the combustion of gasoline and diesel fuels, burning of fossil fuels for electric generation, various industrial processes, and the eruption of volcanoes. SO\(_2\) irritates the eyes and respiratory system, and aggravates respiratory diseases such as asthma and chronic bronchitis. Around non-controlled point source of the pollutant, SO\(_2\) may also cause direct injury to leaves and reduce photosynthesis of sensitive species.

Emissions of sulfur dioxide are chemically transformed to sulfuric acid, which can be partially or completely neutralized by ammonia and other alkaline substances to form sulfate salts. The oxidation of sulfur dioxide to sulfuric acid can occur in the gas phase, the aqueous phase (in rain, cloud, or fog), and the particle phase. During daytime gas-phase reactions, sulfur dioxide is converted to sulfuric acid primarily by reaction with hydroxyl radical. In the aqueous phase, ozone is an important oxidant for sulfur dioxide at high pH. Sulfuric acid adheres very rapidly to existing particles. The US NAAQS for SO\(_2\) has an annual mean of 0.03 ppm, a 24-hour average of 0.14 ppm and a three-hour average of 0.50 ppm. Mexico RAMA has a maximum 24-hour average of 0.13 ppm.

2.4. Tropospheric Ozone

Tropospheric ozone occurs in Earth’s lower atmosphere, and it is the principal component of smog. Ozone is formed by photochemical reaction of NO\(_x\) (Section 2.2) and VOCs emitted by cars, power plants, industrial boilers, refineries, and plants. When inhaled, ozone can cause acute respiratory problems, inflammation of lung tissue, significant temporary reduction in lung capacity, aggravate asthma, and impair the body immune system. Ground level
ozone can also interfere with the ability of plants to produce and store food (e.g., soybeans, kidney beans, wheat, cotton), which compromises growth, reproduction, and overall plant health. It reduces the agricultural yields of many economically important crops such as soybeans, wheat, and cotton. Ozone can also affect ecological functions such as water movement, mineral nutrient cycling and habitats by its cumulative effects on long-lived species such as trees and forest ecosystems.

O₃ concentration is estimated to have increased by 36% since 1750. This increase is due primarily to anthropogenic emissions of several O₃-forming compounds. The monitoring of ozone concentrations in complicated by changing weather patterns often resulting in yearly differences and the fact that ozone and pollutants can be carried to areas hundreds of miles downwind of polluted sources. It is however desirable to achieve some form of monitoring of the global distribution of ozone. National Aeronautics and Space Administration (NASA) sponsorship has enable some research along this line. Also as part of NASA’s Global Tropospheric Experiment (GTE), in situ ozone measurements aboard aircraft have been made since 1982.

Ozone control strategies require knowledge of the species profile of volatile organic compounds, as well as identification and quantification of the various hydrocarbon compounds emitted from both mobile and stationary sources. Typically, VOC emissions profiles do not list the amounts of all organic species emitted and very often they are derived from profiles obtained from other sources that might have incorrect quantities. The US NAAQS is 0.12 parts per million of ozone measured over one hour to a standard of 0.08 parts per million measured over eight hours, with the average fourth highest concentration over a three-year period determining whether an area is out of compliance.

2.5. Particulate Matter

Particulate matter is a mixture of liquid droplets and solid particles found in the atmosphere. The particle sizes are classified by size for the purpose of measurement, emission control, effects, and mitigation strategies. Historically, particles with diameters less than 10 microns (PM-10) have been the major concern, because they can easily pass into the lung. However more recently scientist have labeled particle sizes measuring 2.5 micron (PM-2.5) in diameter and smaller as the most damaging to human health because they penetrate and remain in the deepest passages of the lungs. Particulate matter contains toxic chemicals, some of which are known to cause cancer. They can irritate the respiratory system, accumulate in the lungs to cause silicosis, asbestosis, and aggravate conditions such as asthma and other respiratory disease. PM-10 also interferes with plant photosynthesis. The main sources of PM-10 include carbon used in industrial and domestic combustion gasoline, diesel, industrial processes, and fires, and includes dust, soot, metallic particles, cement, pollen, and organic compounds. The US NAAQS for PM-2.5 is 15 µg/m³ with a 24-hour limit of 65 µg/m³. PM-10 NAAQS is an annual mean of 50 µg/m³ and a 24-hour average of 150 µg/m³. Mexico RAMA has a 24-hour average of 150 µg/m³.

2.6. Measurement Networks
The measurement network for parameters that affect air quality is very comprehensive. The global coverage (particularly in the Northern Hemisphere) is good with very elaborate networks especially in heavily polluted areas such as the Los Angeles, Mexico City, Tokyo, and the UK. Most of these networks are multipurpose in that they are also used to monitor other parameters that are important to phenomena such as climate change. Measurements may be made continuously, integrated, or static. Continuous measurements occur where pollutant concentrations are determined with automated methods and recorded or displayed continuously. For integrated measurements, pollutant concentrations are either determined with automated or manual methods and integrated hourly or daily on a fixed schedule. Static measurements are where pollutant estimates are derived from long-term exposure to qualitative devices or materials. Measurements may vary in scale, from micro, which represents several meters up to 100 meters, to global, which characterizes a nation or the globe as a whole. The particular objective of the monitoring site will dictate the method and equipment used, ranging from collection flask (static concentrations), to probes and manifolds, and open path gas analyzers (mesoscale, 100 meters to 4 km.).

Over 4300 monitoring sites operate in North America, representing air quality monitoring in Canada, the United States, and Mexico. The ambient air monitoring program in the United States is organized and monitored from a number of divisions within (and associated with) the Environment Protection Agency (EPA), including the office of the Air Quality Planning and Standards and the Emission Monitoring and Analysis Division. The monitoring is carried out by state and local agencies and consist of three major categories. The State and Local Air Monitoring Network (SLAMS) consists of ~4000 monitoring stations, the National Air Monitoring Stations (NAMS) has ~1080 stations and is a subset of SLAMS with an emphasis on urban and multisource areas. The Special Purpose Monitoring Stations (SPMS), which are not permanently located and can be adjusted easily to accommodate changing needs, measure the clean-air criteria pollutants.

The National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL), conducts research related to the constituents of the atmosphere that may affect Earth’s climate and the ozone layer. The CMDL Aerosol and Radiation Group studies the behavior of aerosols and radiation. The Ozone and Water Vapor Group looks at stratospheric and tropospheric ozone. The Halocarbons and other Atmospheric Trace Species Group (HATS) quantifies the distribution and magnitudes of the sources and sinks of atmospheric nitrous oxide (N₂O) and halocarbons. The CMDL Carbon Cycle Greenhouse Gas (CCGG) makes flask sample measurements and continuous baseline observation. They maintain reference gases for carbon dioxide (CO₂), methane (CH₄), and carbon monoxide (CO). CMDL HATS group and CCGG operate an extensive measurement network of observatories (for baseline measurements), tall towers, aircraft, balloons, ground-based sites, and commercial ships. Figure 1 shows the CMDL global network, which includes measurements of carbon dioxide, methane, carbon monoxide, hydrocarbons, nitrous oxide, sulfur hexafluoride, and stable isotopes of carbon. This coverage is very extensive, both marine and terrestrial, and represents a comprehensive
global data set. CMDL also uses the Measurement of Air Pollution from Satellite (MAPS) instrument to examine carbon monoxide (CO) mixing ratios using gas filtered correlation radiometry.

Figure 1. NOAA CMDL Carbon Cycle Gasses Group global network, which makes measurements of carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulfur hexafluoride, and stable isotopes of carbon dioxide

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) is a network of over 200 precipitation monitoring sites across the continental United States, Alaska, Puerto Rico, and the Virgin Islands. The network has been operational since 1978 and collects data on the chemistry of precipitation by analyzing for hydrogen, sulfates, nitrates, ammonium chlorides, and base cations. The NADP/NTN sites also include the Mercury Deposition Network and the Atmospheric Integrated Research Monitoring Network.

The State of California in the USA has an extensive monitoring network consisting of monitoring stations operated by the Air Resource Board (ARB), the local Air Pollution Control Districts (APCD), the Air Quality Management Districts (AQMD) by private contractors and by the National Park Service (NPS). The California Air Resources Board is a part of the California Environmental Protection Agency. Their mission is to promote and protect public health, welfare, and ecological resources through the effective and efficient reduction of air pollutants while recognizing and considering the effects on the economy of the State. ARB research has led to significant improvements in air pollution monitoring methods, improved air quality models and more flexible control strategies.

In Mexico, RAMA is the Automated Atmospheric Monitoring Network that operates across the metropolitan area of Mexico City. It is considered to be one of the best air quality monitoring networks in the world, because of its extension and complexity, comparable to networks in Los Angeles, California and Tokyo, Japan. The network consist of 33 stations that provide automated monitoring of CO, SO₂, NO₂, O₃, NOₓ, and hydrogen sulfide (H₂S), as well as manual stations measuring lead and particulate matter among other parameters, and meteorological monitoring.

The United Kingdom (UK) Department of Environment, Transport, and Regions operates an automatic monitoring network consisting of 112 stations both rural (19) and urban (93) areas across the UK. These sites measure a wide range of pollutants such as O₃, NO₂, NO, Noₓ, CO, SO₂, particulates, and many species of hydrocarbons.
The Acid Deposition Monitoring Network in East Asia (EANET) under the auspices of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW), currently operates 38 monitoring stations in ten countries (China, Indonesia, Japan, Republic of Korea, Malaysia, Mongolia, Philippines, Russian Federation, Thailand, and Vietnam) including 16 "remote" sites, seven "rural," and 15 "urban," which measure wet deposition. Ten of these stations also measure atmospheric concentrations of pollutants (using filters), 22 stations measure ozone, nitrous oxides, and sulfur dioxide, and nine stations measure particulate matter. For wet deposition the chemical analysis is carried out for daily or weekly composite samples. Regular data are accessible from most of these stations since March through May 1999.

3. Parameters that Reflect Ecosystem Dynamics

Ecosystem dynamics represent the interrelationship between biotic components and the atmosphere. This takes the form of a feedback cycle, which can result in changes in the environment. Climate change is a primary example, resulting from phenomena such as population increases and the increasing pressures on ecosystem resources, urban sprawl, increased consumption of fossil fuel, and deforestation. These changes are reflected in the increased concentration of trace gasses and aerosols, the primary ones of which are carbon dioxide (CO$_2$), methane (CH$_4$), and nitrous oxide (N$_2$O), and are discussed in further detail below. In order to make informed decisions about our resources, we need to acquire a detailed understanding of the sources, sinks, and the processes of transport and transformation of these compounds and how they interact with and affect atmospheric, biological, and ecological systems.

3.1. Carbon Dioxide

3.1.1. Trends and Estimates

Carbon dioxide is a primary greenhouse gas that has been consistently increasing from a preindustrial revolution concentration of 288 ppm, to current values exceeding 350 ppm. This represents an increase of 31%, which is due primarily to anthropogenic sources. The current CO$_2$ values have not been exceeded for at least the past 420 000 years. Approximately 75% of the increase in atmospheric CO$_2$ is a result of the burning of fossil fuel. Figure 2 shows the concentrations sampled at four long-term sites, and Figure 3 shows the CO$_2$ global average trend and rate of change for the 1980s and 1990s. This trend is expected to continue into the future. Carbon dioxide cycling has profound dynamic impact on our ecosystem, and the many uncertainties surrounding all the feedback components and individual budget compositions in its cycling and estimates, demands continued high priority monitoring of this compound.
Figure 2. Atmospheric carbon dioxide mixing ratios determined from the continuous monitoring programs at the four NOAA CMDL baseline observatories

Figure 3. Global average of atmospheric carbon dioxide mixing ratios determined using measurements from NOAA CMDL cooperative air sampling network

The rate of accumulation of CO₂ in the atmosphere varies on interannual and decadal time scales, and presents a difficulty in quantitatively accounting for observed imbalances in the global carbon budget. The latitudinal trend of CO₂ concentration is shown in Figure 4. The mid latitudes of the Northern Hemisphere has the highest concentrations of CO₂, and has been suggested to be the location of the source of the imbalance in the carbon budget, the "missing sink."

Figure 4. Latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer

The increase in CO₂ concentration is considered primarily responsible for a similar increase observed in global temperature over the same time period. In an effort to define the radiative effects of a given greenhouse gas over a specific time span relative to the effects of carbon dioxide, the IPCC developed an index called the global warming potential (GWP). This is defined as the cumulative radiative forcing between the present and some chosen time horizon caused by a
unit mass of gas emitted now, expressed relative to that for the reference gas CO$_2$, which has a GWP of 1.

3.1.2. Monitoring CO$_2$

There is a long history (since the 1950s) of global CO$_2$ monitoring networks. The Carbon Dioxide Information Analysis Center (CDIAC) is the primary global change data and information analysis center. It is operated by the US Department of Energy (DOE). CDIAC archives data on CO$_2$ and other radiatively active gasses in the atmosphere, acquired from sampling techniques varying from, periodic flask air sampling to continuous concentration sampling (Section 3.4) and historical ice core records. These include the Scripps Institute of Oceanography, which operates four monitoring sites, the NOAA/CMDL flask air sampling network, which has 35 sites, as well as networks and sites in Europe (Umweltbundesamt (UBA) with five sites), Australia (Cape Grim), Canada (Atmospheric Environment Service (AES) with four sites), and five sites from the Main Geophysical Observatory network.

CO$_2$ flux from the ocean and the terrestrial ecosystems represent a large uncertainty when trying to model and balance the global carbon budget. As a result, a series of CO$_2$ flux networks called FLUXNET are operated worldwide, which collect long-term measurements of CO$_2$, water vapor, and energy exchange from a variety of worldwide ecosystems. This is integrated into consistent, quality assured, documented data sets. The aim of FLUXNET is to contribute critical new information to help define CO$_2$ in the global budget and to improve understanding of Net Primary Productivity (NPP) and carbon sequestration for different terrestrial ecosystems.

Major regional networks of FLUXNET are the AmeriFlux network, which consist of 26 sites in the United States, seven in Canada, two in Brazil, and one in Costa Rica. The CARBOEUROPE network consisting of 32 sites in Europe, and the ASIAFLUX network consisting of 15 sites across Asia and 26 in Japan. Recent research developments in South America have added several sites under The Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). These network of monitoring sites continues to expand, and represents a broad cross section of ecosystem types.

3.2. Methane

3.2.1 Trends and Estimates

Methane, a naturally occurring greenhouse gas, has been increasing in the atmosphere since the Industrial Revolution due to anthropogenic activities. Mean global concentrations have increased from a preindustrial level of ~700 parts per billion by volume (ppb) to ~1720 ppb in the mid-1990s. The annual increase in concentrations ranged from 8 – 13 ppb y$^{-1}$ over the period 1980 – 1995. Observations have indicated a decline in the growth rate of methane during the 1990s, therefore, if emissions remain constant, the globally averaged concentrations should reach approximately 1800 ppb within the next few
decades.

Methane concentration levels in the atmosphere have been continuously monitored over the past two decades by the National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL), Carbon Cycle Greenhouse Gases Group’s Cooperative Air Sampling Network. The latitudinal distribution of methane is similar to that of CO$_2$, and is shown in Figure 5. Figure 6 shows the trends in global averages and growth rates since 1984.

![Figure 5. Latitudinal distribution of atmospheric methane in the marine boundary layer](http://www.cmdl.noaa.gov/ccg/figures/figures.html).

![Figure 6. Global average of atmospheric methane mixing ratios determined using measurements from NOAA CMDL cooperative air sampling network](http://www.cmdl.noaa.gov/ccg/figures/figures.html).

The atmospheric lifetime of methane is 12 ± 3 years. It is removed from the atmosphere primarily through oxidation by the hydroxyl radical (OH) resulting in the production of water vapor and peroxy radicals.

CH$_4$ + OH + O$_2$ $\rightarrow$ CH$_3$O$_2$ + H$_2$O

The peroxy radicals are eventually oxidized to produce OH. Under polluted atmospheric conditions, these OH radicals are limited by reactions with NO$_2$, producing nitric acid, and therefore reducing its effectiveness in methane destruction. Over a 20- and 100-year period, methane has a global warming potential of ~56 and 21, respectively, with carbon dioxide having a GWP of 1 for all time periods. It has been estimated that an uncertainty of ±35% exist in each individual gas’s GWPs, not considering the uncertainties in the carbon dioxide reference.

Three global sinks for methane have been identified by IPCC. These are the tropospheric oxidation of methane by OH radical, removal into the stratosphere
and subsequent destruction, and the microbial uptake by soils. By far the greatest sink is the tropospheric oxidation of methane, which accounts for ~88% of the total sink at 490 Tg CH₄ y⁻¹. Stratospheric losses and uptake by soils make up another 7% (40 Tg CH₄ y⁻¹) and 5% (30 Tg CH₄ y⁻¹) of the total sink, respectively. Uncertainties in these estimates range from ±17 to ±50%. Total atmospheric sink is therefore 560 (460 – 660) Tg CH₄ y⁻¹.

The total natural source of methane has been estimated to be ~160 (± 31%) Tg CH₄ y⁻¹. Natural sources include wetlands (72% of the total), termites (13%), oceans (6%), and other unknown sources (9%). Total anthropogenic sources were estimated to emit 375 (± 20%) Tg CH₄ y⁻¹. Anthropogenic sources included fossil fuel related sources that produced an estimated 100 (± 30%) Tg CH₄ y⁻¹, and biospheric sources that emitted ~275 (± 27%) Tg CH₄ y⁻¹. This gives a total source of 535 (410 – 660) Tg CH₄ y⁻¹.

The observed atmospheric increases in methane indicated that sources exceeded sinks by 37 (± 7%) Tg CH₄ y⁻¹. However, balancing the budget from the above estimates of sources and sinks indicates that sinks are greater by 25 Tg CH₄ y⁻¹. This discrepancy is due to the fact that large uncertainties exist in the source and sink estimates, and these uncertainties are more than four times greater than the difference of the two terms. Clearly there is a need to improve the estimated magnitude of each source/sink terms and this represents a serious gap in our knowledge.

With good estimates of the individual sources on a regional scale, countries would be able to target specific sources with varying degrees of mitigation policies suited to their unique condition or situation. The end result would be an overall reduction in emissions from that country or region cumulating to a global reduction in methane emissions.

### 3.2.2. Monitoring Methane

Global atmospheric methane concentration levels have been continuously monitored over the past two decades by the Cooperative Air Sampling Network of the Climate Monitoring and Diagnostics Laboratory of NOAA. The air sampling network consists of 46 land based stations in the Northern Hemisphere, 14 in the Southern Hemisphere, and eight ship-based stations providing a total of 68 monitoring stations around the globe. The ship based stations collect air samples for analysis between New Zealand and North America, and between Hong Kong and Singapore along latitudinal transects. Air samples are collected in flasks once a week on average for the land based sites, and once every week to three weeks on average for ship based stations during campaign periods. The air samples are analyzed for methane using gas chromatography at the NOAA CMDL in Boulder, Colorado.

The IPCC has developed guidelines, based on measured data (and some data from models) reported in the literature and expert opinion, that help countries determine their greenhouse gas inventories. The guidelines can be considered an empirically based regional to global scale emission model since it provides
greenhouse gas emission factors and scaling up procedures for natural and anthropogenic sources. The predicted emissions can be used as input into general circulation models of the atmosphere in order to simulate effects of changing radiative forcing on climate. The IPCC approach lacks regional sensitivity, however individual countries can use the approach as a template and adjust the emission factors, through new research, to reflect their prevailing/changing conditions or practices.

Because methanogenesis in natural systems is governed by the complex interaction of the forcing agents, simplified deterministic relationships are not applicable. Process-based models are therefore better suited to account for the stochastic nature of methanogenesis (over time and space). It is encouraging that their predictions have compared well with measured emissions. A major limitation to their application, however, is the heavy data requirements of some of these models.

Predictions of methane flux to the atmosphere from biomass burning are mainly from empirical models at the ecosystem scale. Emissions are modeled in two steps. The first is to determine the fractions of trace gases emitted from the combustion of different types of biomass (e.g., grasses, crops, types of trees). The next step scales up by estimating the land cover fraction of the various types of biomass that are burned, and the seasonal and spatial distribution of burning episodes.

3.3. Nitrous Oxide

3.3.1. Trends and Estimates

Nitrous oxide, a naturally occurring greenhouse gas, has been increasing in the atmosphere since the industrial revolution. Its increase, however, has not been as dramatic as the other greenhouse gases. Mean global concentration at preindustrial times was ∼275 ppb and has since increased to ∼312 ppb in the mid-1990s (∼17% since 1750). Approximately 33% of these emissions are from anthropogenic sources. The annual concentration increase over the late 1980s to early 1990s has ranged from 0.5 – 0.8 ppb y⁻¹ (an increase of 0.16 – 0.25 % y⁻¹). It was therefore estimated that the atmospheric concentration in 2000 was in the 315 – 316 ppb range.

The atmospheric lifetime of nitrous oxide is ∼120 ± 30 years. Once it has been transported into the stratosphere it is removed from the atmosphere by photolysis and reactions with excited oxygen atoms. This is the main sink. Due to its long atmospheric residence, the GWP of nitrous oxide over a 20 and 100 years period is 280 and 310 times that of CO₂, respectively.

Two global sinks for nitrous oxide have been identified. These are the stratospheric destruction by photodissociation (sunlight in the 180 – 230 nm wavelengths) and reaction with oxygen atoms, and the consumption by certain soils, although this latter sink is uncertain and no global estimates have so far been made. The major sink, therefore, is the stratospheric destruction, which accounts for the current estimated total sink of ∼9 – 16 Tg N y⁻¹. Nitrous oxide
has an additional detrimental role in the atmosphere, in which the stratospheric oxidation of N₂O produces nitric oxide (NO) which in turn reacts strongly with ozone leading to the destruction of this protective trace gas in the stratosphere.

The total natural source of nitrous oxide has been estimated to be ~6 – 9 Tg N y⁻¹. Two natural sources have been identified. The primary source has been attributed to soils (both tropical and temperate) and they account for ~66 – 77 % of the total natural source. Oceans are the remaining source of nitrous oxide. The nitrous oxide flux into the atmosphere was found to be mainly from the dissolved gas in the upper 1000 m of seawater.

Anthropogenic sources of N₂O have been estimated at ~4 – 8 Tg N y⁻¹. Agricultural activities are a significant source of atmospheric N₂O, resulting in ~54 – 75 % of the total anthropogenic contributions. Agricultural sources are cultivated soils and animal excreta management. Other anthropogenic sources include biomass burning (which includes an agricultural component) and industrial processes (fossil fuel combustion, adipic acid (nylon) production, and nitric acid production). The combined anthropogenic and natural sources give a total N₂O source strength of 10 – 17 Tg N y⁻¹.

The observed atmospheric increases in nitrous oxide indicated that sources exceeded sinks by 3.9 Tg N y⁻¹. However, balancing the budget from the given estimates of sources and sinks indicates that sources exceed sinks by only 1 Tg N y⁻¹. This discrepancy is due to the fact that large uncertainties, at present not estimated, exist in the source and sink terms. If we examine the given ranges in the source/sink estimates, then an uncertainty of approximately ± 30% can be given to the means of these ranges. Depending on the magnitude of these source/sink terms, the 30% uncertainty is greater than the 1 Tg N y⁻¹ excess in sources over sinks. Clearly there is a need to improve the estimated magnitude of each source/sink term and this also represents a serious gap in our knowledge.

### 3.3.2. Monitoring Nitrous Oxide

Nitrous oxide concentration levels in the atmosphere have been continuously monitored since 1977 by NOAA CMDL. A total of seven monitoring stations around the globe (South Pole to Northwest Territories, Canada) were employed by the group. Halocarbons and other Atmospheric Trace Species (HATS), is a CMDL program that quantifies the distributions and magnitudes of the sources and sinks for atmospheric N₂O and halogen containing compounds. Measurements are taken from ground-based stations, towers, ocean vessels, aircraft, and balloons, using both flask and gas chromatographic systems. HATS has been collecting air samples in flasks since 1977 from locations in the USA including Hawaii, and the South Pole. Additional sites in Tasmania and the Northwest Territories were added in 1991.

There are two main methods used by researchers to measure nitrous oxide fluxes (emissions) from identified sources. These are chamber or enclosure based and micrometeorological flux observation towers (Section 3.4). Soils have received significant study, primarily agricultural soils because of their potential for
adopting abatement strategies that reduce emissions and for the study of N-cycling in the soil-plant-atmosphere system.

The IPCC has developed empirical models or guidelines to help countries estimate their nitrous oxide emissions. This approach provides emission factors and scaling up procedures for the natural and anthropogenic sources. Similar to methane, however, this methodology lacks sensitivity to climate, prevailing practices and national or regional effects.

The source that has received significant modeling attention is soils. This is because:

(a) there is an understanding of the formation processes involved;
(b) for agricultural soils, we can potentially limit N₂O release into the atmosphere;
(c) fluxes are easily measured for model verification.

The models that have been developed over the past decade are process based in which N-cycling in the soil-plant-atmosphere system is simulated through biophysical-chemical reaction kinetics and gaseous transport into the atmosphere. One difficulty models face is the ability to simulate the emission pulse often seen during spring thaw.

3.4. Methods of Measurement

There are many methods available to researchers to measure atmospheric gas (emissions) from identified sources and sinks. Generally, the methods involve some form of air sampling, with the sampled air then being analyzed for the particular gasses. Usually, observations are taken at the local scale and are then scaled up by an appropriate method of spatial or density integration to obtain budgets at the regional and global scales. This section summarizes the various measurement technologies that have been developed, and highlight the most appropriate or effective measurement tool for a given source or sink.

3.4.1. Global-Scale Observations

The method used to obtain global atmospheric concentrations is a simple, intuitive, and effective technique. The frequency of observations in a year, the number of years in which these observations are made, and the spatial distribution of monitoring stations around the globe provide considerable information on the spatial and temporal trends in concentration levels.

3.4.2. Indirect Budget Methods

The indirect budget method examines the “unaccounted for” gas from such facilities as natural gas plants. This unaccounted gas is the difference between the quantity of gas metered into the facility and the quantity metered out of the facility. However, this approach is insensitive to losses occurring outside of the facilities such as directly from wells, during transit from the wells to the facility, and once the gas leaves the facility, which introduces large uncertainties in the estimates.
3.4.3. Mass Balance Methods

Gas concentrations in the atmosphere coming into and exiting a facility or advection by a location, can be measured. Such a mass balance technique can be effectively used, for example, to quantify the production of methane and carbon dioxide from dairy cows housed in barns. Sophisticated monitoring systems can be installed to continuously sample air at every ventilation intake and exhaust outlet in the barns. These air samples can then be analyzed during the sampling process (i.e., on-line) for methane and carbon dioxide concentrations. Similar method can also be used to estimate emissions from deep coal mines. The mass balance method can be tested by releasing known quantities of a tracer gas.

3.4.4. Flask Sampling

Flask sampling technique requires guidelines on wind speeds, direction and time of day for sample collection. Whole air samples are always collected (no removal of water vapor) in pairs once or twice a week. The samples are then dried during analysis, using a cryogenic trap at −70 °C. The apparatus used for collecting samples went from cylindrical glass flask in 1967 to hand held aspirators in 1968 – 1980 and ultimately to portable samplers with a larger battery, rugged pump, and back pressure regulator.

3.4.5. Chamber or Enclosure Methods

Enclosure methods are a simple, adaptable, and popular way of measuring gas fluxes from small localized areas. They are particularly useful in measuring very small fluxes and deployment in complex surface terrain. They are relatively low cost, simple to set up, and portable. These major advantages have resulted in chambers being applied in many different situations. Examples of the use of enclosure methods are ventilated head hoods and face masks for measuring methane emissions from individual cows, chambers used to measure methane fluxes from manure slurries and over the soil-atmosphere interface, N₂O and CO₂ from agricultural and forested soils, bogs, fens, and waterlogged drainage ditches.

In general, there are two types of chambers, static and dynamic, with various hybrids of either technology. Static chambers are the simplest form of chamber technology. Air samples are taken from the enclosed air space over a short duration (less than 30 minutes) at discrete time intervals (usually not more than 10 minutes apart) from the time the chamber is sealed. These samples are then analyzed, usually by gas chromatography, in the laboratory. The gas flux is determined by the rate of change in concentration over time. Dynamic (or steady-state) chambers attempt to maintain the environmental or micrometeorological conditions prevailing outside of the chamber within the enclosure. These chambers are generally transparent to allow photosynthesis to continue, and the temperature, humidity, and carbon dioxide levels regulated to match outside conditions. They can also be ventilated. For sealed dynamic chambers, fluxes are determined in a similar fashion as for the static chambers. For ventilated chambers, the flux is determined by the total air exchanged through the chamber and the difference in concentrations between the incoming
and exhausted air.

There are two major disadvantages of the chamber technique. One is the natural conditions are modified by the enclosure. This is minimized in dynamic chambers but not altogether removed. For animals, they are subjected to an altered environment that may introduce an artificial stress resulting in biased responses and observations. For other systems, the chamber modifies the microclimate of the enclosed area, which can affect the physical, biochemical and physiological responses of the system. This is the main reason why air sampling is conducted over a limited period, particularly for static chambers. The other disadvantage is that the spatial and temporal variability of emissions cannot be adequately accounted for without the deployment and continuous sampling of large numbers of chambers. Emission measurements from a few animals over a limited time period cannot be confidently scaled up to give annual emission estimates for the entire population of similar animals. Trace gas emissions from ecosystems are also spatially and temporally intermittent, often with localized "hot spots." When a small number of chambers are deployed, placement of a chamber on such a “spot” and/or if the frequency of sampling is limited then the overall mean emissions can be skewed.

3.4.6. Micrometeorological Methods

The main advantages of micrometeorological methods are that they offer continuous and spatially integrated flux observations representing relatively large areas that are on the order of square kilometers. The apparatus includes an observation platform such as a tower, balloon, or aircraft on which sensors are mounted that measure wind velocities and direction, air temperatures, and trace gases. For a tower these sensors can be mounted at various heights, whereas for an aircraft or balloon observations are made sequentially at different heights. Air samples are either analyzed on- or off-line, however, the increasing use of tunable diode laser trace gas analyzers have resulted in more use of on-line methods. Detailed micrometeorological observations are made in order to calculate surface aerodynamic properties necessary for flux determination. Two main approaches exist, they are the gradient method and the eddy correlation method.

The gradient method involves taking air samples from at least two heights sufficiently far apart to detect a concentration gradient. The concentration gradient is then used in established micrometeorological flux gradient relationships to calculate the flux. The eddy correlation technique determines the flux by calculating the covariance between the concentration fluctuations of the trace gas and the fluctuations in the vertical component of the wind velocity. This requires fast response three dimensional wind velocity anemometers and gas analyzers. Generally only one sampling height is necessary for eddy correlation; it is therefore more favorable for aircraft platforms.

An alternative approach, which has been explored especially for trace gasses such as methane, is the use of an atmospheric diffusion model to back-calculate the emission strength from measured downwind concentration data. This approach has been used to estimate methane emissions from landfills in Tokyo,
to measured cross-wind methane concentration profile downwind of landfills, as well as in a Gaussian plume model to estimate emission strengths. A combined mass balance and one-dimensional constant-source diffusion modeling approach has been used to estimate methane flux from a large coastal area of northern Britain using an aircraft platform. Vertical and cross-wind concentration profiles have also been measured with this method both upwind and downwind of peat bogs and agricultural sources.

The relatively high cost and sophistication in instrumentation and set up are major disadvantages of micrometeorological methods. In addition to this, the method requires that platforms be set up in a uniform terrain with an adequate upwind fetch. The adequate fetch ensures that the aerodynamic properties of the terrain and air flow, which the methods depend upon, are stable and not chaotic. Observations cannot be made in locations of turbulent chaotic flows such as in urban centers, and are very difficult in mountainous terrain, or within a forest or crop canopy.

3.4.7. Atmospheric Tracer Method

For this method, a tracer gas is released from the source area of the compound being studied (such as methane), and the downwind atmospheric concentrations of the two gases are measured (at the same location). Provided that both gases undergo similar atmospheric transport (diffusion), the methane source strength ($Q_{CH4}$) for example, can be estimated by a simple ratio technique from the known tracer gas emission strength ($Q_{tracer}$), and the measured concentrations. The following relationship is used:

$$Q_{CH4} = Q_{tracer} \times \frac{C_{CH4}}{C_{tracer}}$$

where $C_{CH4}$ and $C_{tracer}$ are the downwind concentrations of methane and tracer gas, respectively. A popular tracer gas is sulfur hexafluoride ($SF_6$) because of its low background concentration (~5 parts per trillion), easy detection, and inert properties. However, $SF_6$ is a potent greenhouse gas with a GWP of 23 900 over a 100-year time period, and a lifetime of ~3200 years.

This method has been used to estimate emissions from a wide range of sources such as methane emissions from dairy herds and manure slurry tanks, free ranging sheep and dairy cattle, landfill, leakage from natural gas facilities, and from small cities. This method is considered a powerful tool for providing good estimates of emissions from complex sources. The major advantage of this technique is that no meteorological parameters need to be measured or used and no diffusion modeling is required. It is therefore particularly useful for sources located in complex aerodynamic flows where current dispersion theories are inadequate or inappropriate.

3.5. Radiation and Boundary Layer Properties

This article is not complete without comments on the constant and ongoing
necessity for radiation and atmospheric boundary layer properties. The atmospheric parameters discussed above are used in a variety of ways. They are most commonly used as inputs into models for predictive, management, or mitigative purposes. In order to effectively, accurately, and efficiently use these parameters, some information is needed on radiation conditions (both short and long wave), and characteristics of the atmospheric boundary layer. Traditionally, large-scale synoptic/generalized conditions have been used in models. Over the past decade, however, these models (atmospheric circulation, climate, pollution, CO₂, methane, for example) have become increasingly more sophisticated in the number of atmospheric layers and physical components they include as well as increased spatial and temporal resolution. As these models attempt to incorporate the lower layer (surface layer) of the atmosphere, more heterogeneous conditions need to be addressed, as the surface impacts the atmospheric circulation and exchange.

In addition to long- and shortwave radiation, global vertical profiles of temperature, pressure, and/or density, actual winds (if a satisfactory way to do it is found) and column-integrated water vapor and liquid water would be high priority. Long term stability would be required for these observations to be useful for climate/climate change. Micrometeorological monitoring networks such as FLUXNET, documents most of these parameters routinely. Expansion of these types of monitoring network will ensure more global coverage for these parameters. The limitation of these networks for providing global monitoring of these atmospheric parameters is their lack of coverage in areas such as Africa, which is not a high priority area for the monitoring of CO₂ flux. There are no long term monitoring FLUXNET sites on the African continent, and only recently has there been expansion on the South American continent.

4 Conclusion

The variability of both atmospheric and surface condition globally, and our inability to properly capture the details of the complex interactions of the important atmospheric constituents, dictates that a hierarchy of measurements is necessary. This has been, to some extent, the template for several large scale international projects that have been focused on ecologically and climatically significant global ecosystems. The atmospheric parameters that adversely affect our life supporting environment are, for the most part well established. Understanding the way in which they interact with the different components of different ecosystems, at different spatial and temporal scales requires constant, integrated and long-term monitoring. Only in doing so can we hope to make accurate representations in the models we develop to assist us in managing and mitigating their adverse effects on our life supporting system.

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Glossary

Aerosol: A suspension of fine (0.001 to 10 micrometers) solid or liquid particles in air.

Anthropogenic: Conditions resulting from human activities.

Biospheric: Biologically influenced land surface properties.

Atmospheric boundary layer: The lower section of the troposphere (up to ~3 km) that is directly influenced by the presence of Earth's surface, and responds to surface forcing with a timescale equal to or less than one hour.

Climate change: Climate change on the global scale refers to changes in the climate of Earth as a whole, while for a regional, refers to a change in the average weather of that region.

Ecophysiological parameters: Parameters that reflect the interrelationships between the physiological physical, biological, and climatic conditions of an ecosystem.

Ecosystem: A group of communities of organisms and their environment, which functions as an ecological unit in nature.

Greenhouse gas: Gases that have the ability to trap solar radiation in the atmosphere resulting in an increase in the atmospheric temperature.

Methanogenesis: The decomposition of organic matter by bacteria, usually under anaerobic conditions, resulting in the production of methane.

Micrometeorology: Meteorological phenomenon with space scales smaller than ~3 km and timescales shorter than about one hour, and occurs within the atmospheric boundary layer.

Net primary productivity: The net amount of carbon captured by plants through photosynthesis, usually calculated annually.

Photodissociation: The dissociation of the molecules of a substance by the absorption of radiant energy.

Photolysis: Chemical decomposition by radiant energy.

Radiative forcing: The change in the net downward flux of radiation at the top of the troposphere.

Sink: That portions of the surface that absorbs a particular compound is a sink for that compound.

Source: That portion of the surface that gives off a compound is a source for that compound.

Surface layer: The lower portion of the atmospheric boundary layer, typically up to ~100 meters.

Troposphere: The lower part of Earth's atmosphere with an average depth of 1 km.


[These three IPCC reports provide the current level of knowledge on global greenhouse gases, sources and sinks, and emission factors].


Biographical Sketches

**Dr Brown** is a Senior Research Associate for NSF supported Science and Technology Center on Sustainability of Semi-Arid Hydrology and Riparian Areas (SAHRA), in the Department of Hydrology and Water Resources, at the University of Arizona. She received her B.A. from the University of Windsor in 1991, an M.Sc. from McGill University in 1994 and a Ph.D. from McGill University in 1999. Dr Brown is a Co-Investigator in the Mackenzie GEWEX Study (MAGS), a series of large-scale hydrological and related atmospheric and land-atmosphere studies conducted within the Mackenzie Basin of Canada, coordinates the research projects related to the components of the water balance within SAHRA, and operates a subalpine micrometeorological network for monitoring and modeling surface atmosphere exchange, energy balance, and evapo-transpiration/sublimation as they impact snow accumulation, distribution, and melt. She is a member of the UA's Committee on Global Change, which offers an interdisciplinary Ph.D. minor in Global Change, and SAHRA integration committee for multi-institutional interdisciplinary research.

**Dr. Kaharabata** obtained his B.Sc. in mathematics and meteorology from the University of the West Indies, an M.Sc. and a Ph.D. from McGill University, where his research work investigated the turbulent atmospheric transport of trace gases, in particular greenhouse gases, from their sources with the purpose of estimating the strength of the source(s) using nondisturbing methods. Currently Dr Kaharabata is working on research projects with Agriculture and Agri-Food Canada, that deal with estimating the present and future magnitude of greenhouse gas emissions and understanding their production in the agricultural sector. He is involved in the modeling of nitrous oxide emissions from the cultivated soils of Canada, and the development of an agricultural greenhouse gas database. His research interests lie in the areas of measuring and modeling atmospheric trace gas emissions from their sources, and the modeling of turbulent atmospheric transport processes.

**Dr. Bales**, Professor of Hydrology and Water Resources at the University of Arizona, received his B.S. from Purdue University in 1974, an M.Sc. from the University of California, Berkeley in 1975 and his Ph. D. from the California Institute of Technology in 1985. He worked as a consulting engineer from 1975 to 1980, and has taught at the University of Arizona since 1984. He has published extensively in diverse fields of research including alpine hydrology and
biogeochemistry, polar snow and ice, biocolloid transport in porous media, sorption of organic contaminants, coagulation, and mineral weathering. Dr. Bales is currently director of the UA's NASA-supported Regional Earth Science Applications Center (RESAC), Deputy Director of the UA's NSF-supported Science and Technology Center on Sustainability of Semi-Arid Hydrology and Riparian Areas (SAHRA), and Principal Investigator on the UA's Climate Assessment for the Southwest Project (CLIMAS). He is actively involved in research in the Southwestern US, Greenland and Antarctica. Professionally, Dr. Bales is a member of the American Geophysical Union's, Hydrology Section executive committee, is on the editorial board for Eos and is involved in several activities serving the hydrology community. He is a member of the UA's Committee on Global Change, which offers an interdisciplinary Ph. D. minor in Global Change, the UA's Committee on Remote Sensing and Spatial Analysis, and is on the executive committee of the university's Institute for Study of Planet Earth, which provides an interdisciplinary framework for addressing environmental questions.

To cite this chapter
Measurement Programs

NOAA CMDL Carbon Cycle Greenhouse Gases

Figure 1. NOAA CMDL Carbon Cycle Gasses Group global network which makes measurements of carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulphur hexaflouride and stable isotopes of carbon dioxide.

Source: http://www.cmdl.noaa.gov/eg/figures/figures.html
Monthly Mean Carbon Dioxide
NOAA CMDL Carbon Cycle Greenhouse Gases

Figure 2. Atmospheric carbon dioxide mixing ratios determined from the continuous monitoring programs at the 4 NOAA CMDL baseline observatories.
Carbon Dioxide Measurements
NOAA CMDL Carbon Cycle Greenhouse Gases

Figure 3. Global average of atmospheric carbon dioxide mixing ratios determined using measurements from NOAA CMDL cooperative air sampling network.
Figure 4. Latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer.
Global Distribution of Atmospheric Methane
NOAA CMDL Carbon Cycle Greenhouse Gases

Figure 5. Latitudinal distribution of atmospheric methane in the marine boundary layer.
Figure 6. Global average of atmospheric methane mixing ratios determined using measurements from NOAA CMDL cooperative air sampling network.