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 (CO_2), methane (CH_4), nitrous oxide (N_2O), tropospheric ozone (O_3), 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_x) increased by 690%, volatile organic compounds (VOC) increased by 260%, and sulfur dioxide (SO_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_2) by 14%, ozone (O_3) by 6%, particulate matter (PM-10) by 22%, sulfur dioxide (SO_2) by 37%, and in emissions of CO (6%), Pb (32%), NO_2 (3%), VOC (9%), PM-10 (17%), and SO_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_x, O_3, Pb, PM, and sulfur oxides (SO_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. 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 peroxy 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.

O_3 concentration is estimated to have increased by 36% since 1750. This increase is due primarily to anthropogenic emissions of several O_3-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 $\mu g/m^3$ with a 24-hour limit of 65 $\mu g/m^3$. PM-10 NAAQS is an annual mean of 50 $\mu g/m^3$ and a 24-hour average of 150 $\mu g/m^3$. Mexico RAMA has a 24-hour average of 150 $\mu g/m^3$.

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 phenomenon 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 longterm 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.

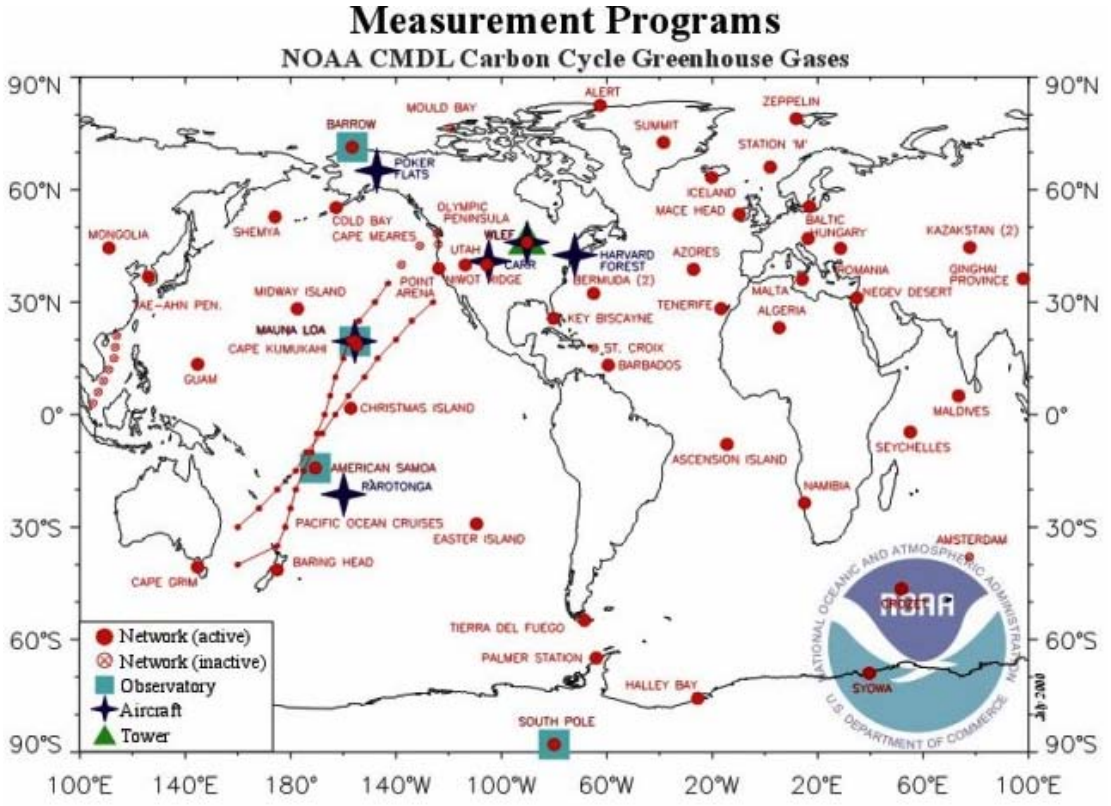

Figure 1. NOAA CMDL Carbon Cycle Gasses Group global network, which makes measurements of carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulfur hexafloride, and stable isotopes of carbon dioxide
Source: <http://www.cmdl.noaa.gov/ccg/figures/figures.html>.

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 (N_2O) and halocarbons. The CMDL Carbon Cycle Greenhouse Group (CCGG) makes flask sample measurements and continuous baseline observation. They maintain reference gases for carbon dioxide (CO_2), methane (CH_4), 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 hexafloride, 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.

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, SO_2, NO_2, O_3, NO_x, and hydrogen sulfide (H_2S), 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 O_3, NO_2, NO, No_x, CO, SO_2, 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.

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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.