Atmospheric Concentrations of Greenhouse Gases

Identification

1. Indicator Description

This indicator describes how the levels of major greenhouse gases (GHGs) in the atmosphere have changed over geological time and in recent years. Changes in atmospheric GHGs, in part caused by human activities, affect the amount of energy held in the Earth-atmosphere system and thus affect the Earth's climate.

Components of this indicator include:

- Global atmospheric concentrations of carbon dioxide over time (Figure 1)
- Global atmospheric concentrations of methane over time (Figure 2)
- Global atmospheric concentrations of nitrous oxide over time (Figure 3)
- Global atmospheric concentrations of selected halogenated gases over time (Figure 4)

2. Revision History

April 2010: Indicator posted
December 2011: Updated with data through 2010
May 2012: Updated with data through 2011
July 2012: Added nitrogen trifluoride to Figure 4
August 2013: Updated indicator on EPA's website with data through 2012

Data Sources

3. Data Sources

Ambient concentration data used to develop this indicator were taken from the following sources:

Figure 1. Global Atmospheric Concentrations of Carbon Dioxide Over Time

- EPICA Dome C, Antarctica: approximately 647,426 BC to 411,548 BC—Siegenthaler et al. (2005)
- Vostok Station, Antarctica: approximately 415,157 BC to 339 BC—Barnola et al. (2003)
- EPICA Dome C, Antarctica: approximately 9002 BC to 1515 AD—Flückiger et al. (2002)
- Law Dome, Antarctica, 75-year smoothed: approximately 1010 AD to 1975 AD—Etheridge et al. (1998)
- Siple Station, Antarctica: approximately 1744 AD to 1953 AD—Neftel et al. (1994)
- Mauna Loa, Hawaii: 1959 AD to 2012 AD—NOAA (2013a)
- Barrow, Alaska: 1974 AD to 2011 AD; Cape Matatula, American Samoa: 1976 AD to 2011 AD; South Pole, Antarctica: 1976 AD to 2011 AD—NOAA (2012)
- Cape Grim, Australia: 1992 AD to 2006 AD; Shetland Islands, Scotland: 1993 AD to 2002 AD—Steele et al. (2007)

- Lampedusa Island, Italy: 1993 AD to 2000 AD—Chamard et al. (2001)

Figure 2. Global Atmospheric Concentrations of Methane Over Time

- EPICA Dome C, Antarctica: approximately 646,729 BC to 1888 AD—Spahni et al. (2005)
- Vostok Station, Antarctica: approximately 415,172 BC to 346 BC—Petit et al. (1999)
- Greenland GISP2 ice core: approximately 87,798 BC to 8187 BC; Byrd Station, Antarctica: approximately 85,929 BC to 6748 BC; Greenland GRIP ice core: approximately 46,933 BC to 8129 BC—Blunier and Brook (2001)
- EPICA Dome C, Antarctica: approximately 8945 BC to 1760 AD—Flückiger et al. (2002)
- Law Dome, Antarctica: approximately 1008 AD to 1980 AD; various Greenland locations: approximately 1075 AD to 1885 AD—Etheridge et al. (2002)
- Greenland Site J: approximately 1598 AD to 1951 AD—WDCGG (2006)
- Cape Grim, Australia: 1984 AD to 2011 AD—NOAA (2013c)
- Mauna Loa, Hawaii: 1987 AD to 2012 AD—NOAA (2013d)
- Shetland Islands, Scotland: 1993 AD to 2001 AD—Steele et al. (2002)

Figure 3. Global Atmospheric Concentrations of Nitrous Oxide Over Time

- Greenland GISP2 ice core: approximately 104,301 BC to 1871 AD; Taylor Dome, Antarctica: approximately 30,697 BC to 497 BC—Sowers et al. (2003)
- EPICA Dome C, Antarctica: approximately 9000 BC to 1780 AD—Flückiger et al. (2002)
- Antarctica: approximately 1756 AD to 1964 AD—Machida et al. (1995)
- Antarctica: approximately 1903 AD to 1976 AD—Battle et al. (1996)
- Cape Grim, Australia: 1979 AD to 2011 AD—AGAGE (2012)
- South Pole, Antarctica: 1998 AD to 2012 AD; Barrow, Alaska: 1999 AD to 2012 AD; Mauna Loa, Hawaii: 2000 AD to 2012 AD—NOAA (2013e)

Figure 4. Global Atmospheric Concentrations of Selected Halogenated Gases, 1978–2012

Global average atmospheric concentration data for selected halogenated gases were obtained from the following sources:

- National Oceanic and Atmospheric Administration (NOAA, 2013b) for halon-1211.
- Arnold (2013) for nitrogen trifluoride.
- Advanced Global Atmospheric Gases Experiment (AGAGE, 2013) for all other species shown.

A similar figure based on AGAGE data appeared in the Intergovernmental Panel on Climate Change's (IPCC's) Fourth Assessment Report (see Figure 2.6 in IPCC, 2007).

4. Data Availability

The data used to develop Figures 1, 2, and 3 of this indicator are publicly available and can be accessed from the references and websites listed in Section 3. There are no known confidentiality issues.

Data for all gases in Figure 4, with the exception of halon-1211 and nitrogen trifluoride, were downloaded from the AGAGE website at: http://agage.eas.gatech.edu/data_archive/global_mean/.

Additional historical monthly data for some of these gases were provided in spreadsheet form by Dr. Ray Wang of the AGAGE project team (AGAGE, 2011). Bimonthly data for halon-1211 were provided in spreadsheet form by Dr. Stephen Montzka of NOAA (NOAA, 2013b). NOAA's website (www.esrl.noaa.gov/gmd/hats/) provides access to underlying station-specific data and selected averages, but does not provide the global averages that are shown in Figure 4. Nitrogen trifluoride data are based on measurements that were originally published in Arnold et al. (2013) and subsequently updated by the lead author (Arnold, 2013).

Methodology

5. Data Collection

This indicator shows trends in atmospheric concentrations of several major GHGs that enter the atmosphere at least in part because of human activities: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and selected halogenated gases. This indicator aggregates comparable, high-quality data from individual studies that each focused on different locations and time frames. Recent data (since the mid-20th century) come from global networks that use standard monitoring techniques to measure the concentrations of gases in the atmosphere. Older data come from ice cores—specifically, measurements of gas concentrations in air bubbles that were trapped in ice at the time the ice was formed. Scientists have spent years developing and refining methods of measuring gases in ice cores as well as methods of dating the corresponding layers of ice to determine their age. Ice core measurements are a widely used method of reconstructing the composition of the atmosphere before the advent of direct monitoring techniques.

This indicator presents a compilation of data generated by numerous sampling programs. The citations listed in Section 3 describe the specific approaches taken by each program. Gases are measured by mole fraction relative to dry air.

Most of the GHGs presented in this indicator are considered to be well-mixed globally, due in large part to their long residence times in the atmosphere. Thus, while measurements over geological time tend to be available only for regions where ice cores can be collected (e.g., the Arctic and Antarctic regions), these measurements are believed to adequately represent concentrations worldwide. Recent monitoring data have been collected from a greater variety of locations, and the results show that concentrations and trends are indeed very similar throughout the world, although relatively small variations can be apparent across different locations.

Most of the gases shown in Figure 4 have been measured around the world numerous times per year. One exception is nitrogen trifluoride, which is an emerging gas of concern for which measurements are not yet widespread. The curve for nitrogen trifluoride in Figure 4 is based on samples collected in Australia and California between 1995 and 2010, plus samples collected approximately monthly in California since 2010. Measurements of air samples collected before 1995 have also been made, but they are not shown in this figure because larger gaps in time exist between these measurements.

Nitrogen trifluoride was measured via the Medusa gas chromatography with mass spectrometry (GCMS) system, with refinements described in Weiss et al. (2008), Arnold et al. (2012), and Arnold et al. (2013). Mole fractions of the other halogenated gases were collected via AGAGE's Medusa GCMS system or similar methods employed by NOAA.

6. Indicator Derivation

EPA obtained and compiled data from the various GHG measurement programs and plotted these data in graphs. Figures 1, 2, and 3 plot data at annual or lower resolution; with ice cores, consecutive data points are often spaced many years apart. Figure 4 plots data at sub-annual intervals. EPA used the data exactly as reported by the organizations that collected them, with the following exceptions:

- Some of the recent time series for CO_2, CH_4, and N_2O consisted of monthly measurements. EPA averaged these monthly measurements to arrive at annual values to plot in the graphs. A few years did not have data for all 12 months. If at least nine months of data were present in a given year, EPA averaged the available data to arrive at an annual value. If fewer than nine monthly measurements were available, that year was excluded from the graph.
- Some ice core records were reported in terms of the age of the sample or the number of years before present. EPA converted these dates into calendar years.
- A few ice core records had multiple values at the same point in time (i.e., two or more different measurements for the same year). These values were generally comparable and never varied by more than 4.8 percent. In such cases, EPA averaged the values to arrive at a single atmospheric concentration per year.
- Although measurements have been made of nitrogen trifluoride in air samples collected before 1995, EPA elected to start the nitrogen trifluoride time series at 1995 because of large time gaps between measurements prior to 1995. The individual data point for 1995 is not shown because it falls below the scale of Figure 4's y-axis.

Figures 1, 2, and 3 label each trend line according to the location where measurements were collected. No methods were used to portray data for locations other than where measurements were made. However, the indicator does imply that the values in the graphs represent global atmospheric concentrations—an appropriate assumption because the gases covered by this indicator have long residence times in the atmosphere and are considered to be well-mixed. In the indicator text, the Key Points refer to the concentration for the most recent year available. If data were available for more than one location, the text refers to the average concentration across these locations.

Figure 4 presents one trend line for each halogenated gas, and these lines represent average concentrations across all measurement sites worldwide. These data represent monthly average mole fractions for each species, with two exceptions: halon-1211 data are only available at two-month intervals, and nitrogen trifluoride measurements were converted into global annual average mole fractions using a model described in Arnold et al. (2013). This update of nitrogen trifluoride represents a change from the version of this indicator that EPA initially published in December 2012. At the time of the December 2012 version, modeled global annual average mole fractions had not yet been published in the literature, so EPA's indicator instead relied upon individual measurements of nitrogen trifluoride that were limited to the Northern Hemisphere.

Data are available for additional halogenated species, but to make the most efficient use of the space available, EPA selected a subset of gases that are relatively common, have several years of data available, show marked growth trends (either positive or negative), and/or collectively represent most of the major categories of halogenated gases. The inclusion of nitrogen trifluoride here is based on several factors. Like perfluoromethane (PFC-14 or CF_4), perfluoroethane (PFC-116 or C_2F_6), and sulfur hexafluoride, nitrogen trifluoride is a widely produced, fully fluorinated gas with a very high 100-year

global warming potential (17,200) and a long atmospheric lifetime (740 years). Nitrogen trifluoride has experienced a rapid increase in emissions (i.e., more than 10 percent per year) due to its use in manufacturing semiconductors, flat screen displays, and thin film solar cells. It began to replace perfluoroethane in the electronics industry in the late 1990s.

To examine the possible influence of phase-out and substitution activities under the Montreal Protocol on Substances That Deplete the Ozone Layer, EPA divided Figure 4 into two panels: one for substances officially designated as "ozone-depleting" and one for all other halogenated gases.

No attempt was made to project concentrations backward before the beginning of the ice core record (or the start of monitoring, in the case of Figure 4) or forward into the future.

7. Quality Assurance and Quality Control

The data for this indicator have generally been taken from carefully constructed, peer-reviewed studies. Quality assurance and quality control procedures are addressed in the individual studies, which are cited in Section 3. Additional documentation of these procedures can be obtained by consulting with the principal investigators who developed each of the data sets.

Analysis

8. Comparability Over Time and Space

Data have been collected using a variety of methods over time and space. However, these methodological differences are expected to have little bearing on the overall conclusions for this indicator. The concordance of trends among multiple data sets collected using different program designs provides some assurance that the trends depicted actually represent atmospheric conditions, rather than some artifact of sampling design.

The gases covered in this indicator are all long-lived GHGs that are relatively evenly distributed globally. Thus, measurements collected at one particular location have been shown to be representative of average concentrations worldwide.

9. Sources of Uncertainty

Direct measurements of atmospheric concentrations, which cover approximately the last 50 years, are of a known and high quality. Generally, standard errors and accuracy measurements are computed for the data.

For ice core measurements, uncertainties result from the actual gas measurements as well as the dating of each sample. Uncertainties associated with the measurements are believed to be relatively small, although diffusion of gases from the samples might also add to the measurement uncertainty. Dating accuracy for the ice cores is believed to be within plus or minus 20 years, depending on the method used and the time period of the sample. However, this level of uncertainty is insignificant when considering that some ice cores characterize atmospheric conditions for time frames more than 100,000 years ago. The original scientific publications (see Section 3) provide more detailed information on the estimated uncertainty within the individual data sets.

Visit the Carbon Dioxide Information Analysis Center (CDIAC) website
(http://cdiac.esd.ornl.gov/by_new/bysubjec.html#atmospheric) for more information on the accuracy
of both direct and ice core measurements.

Overall, the concentration increase in GHGs in the past century is far greater than the estimated
uncertainty of the underlying measurement methodologies. Otherwise stated, it is highly unlikely that
the concentration trends depicted in this indicator are artifacts of uncertainty.

10. Sources of Variability

Atmospheric concentrations of GHGs vary with both time and space. However, the data on atmospheric
GHG concentrations have extraordinary temporal coverage. For carbon dioxide, methane, and nitrous
oxide, concentration data span several hundred thousand years; and for the halogenated gases, data
span virtually the entire period during which these largely synthetic gases were widely used. While
spatial coverage of monitoring stations is more limited, most of the GHGs presented in this indicator are
considered to be well-mixed globally, due in large part to their long residence times in the atmosphere.

11. Statistical/Trend Analysis

This indicator presents a time series of atmospheric concentrations of GHGs. No statistical techniques or
analyses were used to characterize the long-term trends or their statistical significance.

12. Data Limitations

Factors that may impact the confidence, application, or conclusions drawn from this indicator are as
follows:

1. This indicator does not track water vapor because of its spatial and temporal variability. Human
   activities have only a small direct impact on water vapor concentrations, but there are
   indications that increasing global temperatures are leading to increasing levels of atmospheric
   humidity (Dai et al., 2011).
2. Some radiatively important atmospheric constituents that are substantially affected by human
   activities (such as tropospheric ozone, black carbon, aerosols, and sulfates) are not included in
   this indicator because of their spatial and temporal variability.
3. This indicator includes several of the most important halogenated gases, but some others are
   not shown. Many other halogenated gases are also GHGs, but Figure 4 is limited to a set of
   common examples that represent most of the major types of these gases.
4. Ice core measurements are not taken in real time, which introduces some error into the date of
   the sample. Dating accuracy for the ice cores ranges up to plus or minus 20 years (often less),
   depending on the method used and the time period of the sample. Diffusion of gases from the
   samples, which would tend to reduce the measured values, could also add a small amount of
   uncertainty.

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