

Scripps Carbon Dioxide and Oxygen Programs Ralph F. Keeling, PI, Scripps Institution of Oceanography, UCSD, La Jolla, CA

INTRODUCTION

The Scripps CO₂ program was initiated in 1956 by Charles David Keeling and operated under his direction until his passing in 2005. It is currently being continued by Ralph F. Keeling, who also runs the parallel Scripps O₂ program. The combined programs are sustaining the longest continuous measurements of changes in atmospheric carbon dioxide concentration, the isotopes of CO₂, and the atmospheric O₂ concentration (as O_2/N_2 ratio). The program involves flask collections made through cooperative programs with field stations at roughly a dozen stations around the world. The emphasis in the program is in the detection of global and hemispheric trends in these species.

SCRIPPS SAMPLING NETWORK



Station symbols: ALT = Alert; PTB = Point Barrow; CBA = Cold Bay; LJO = La Jolla; BCS = Baja California Sur ; KUM = Cape Kumukahi ; MLO = Mauna Loa Observatory; CHR = Christmas Island; SAM = Samoa; KER = Kermadec; CGO = Cape Grim; NZD = New Zealand ; PSA = Palmer Station ; SPO = South Pole

2 MAUNA LOA CO, RECORD





Observations of ¹⁴C/¹²C ratio expressed as Δ^{14} C from CO₂ samples collected at La Jolla. The analyses were made in collaboration with Thomas Guilderson at the Center for Accelerator Mass Spectrometry at the Lawrence Livermore National Laboratory. The downward trend is the result of the redistribution of bomb ¹⁴C into the oceans and land biosphere. The trend is also influenced by the rate of fossil-fuel burning.

Scripps CO₂ Program - www.scrippsco2.ucsd.edu

Scripps O₂ Program - http://bluemoon.ucsd.edu

CO, TREND



6 ¹³C/¹²C TREND

concentrations.

The ¹³C/¹²C isotopic ratio, expressed as δ^{13} C (in per mil from isotope standard PDB), for the same stations as in the CO₂ trend figure. The dots indicate monthly averages. The oscillating curves are fits similar to those in the CO₂ trend figure. Note the expanded time-scale and inverted isotopic scale (the latter so that phasing is seen to be similar to that of the CO₂ concentration). The ¹³C/¹²C data contain useful constraints on changes in metabolic activity and sources and sinks of CO_2 , with the land biota.

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5 O, TREND

Atmospheric O₂ concentration (reported as O_2/N_2 ratio) from flasks collected in the Scripps O₂ sampling network. Each point represents monthly mean. The O₂ trends tend to mirror the \tilde{CO}_{2} , trends, with an opposing seasonal cycle and long-term trend. The rate of O_{2} loss helps to establish the relative magnitude of the land and ocean sinks for CO, globally. The seasonal cycle contains information about rates of metabolic activity in both the land and ocean biospheres

The ¹⁸O/¹⁶O isotopic ratio, expressed as δ^{18} O (in per mil, positive upwards) for South Pole (SPO, 90°S) and Alert (ALT, 82°N). The ¹⁸O/¹⁶O ratio is sensitive to the gross (i.e. back and forth) exchanges of CO_{2} with the land biosphere and to the distribution of water isotopes driven by hydrological cycle. Note the coherent interannual variations at these stations, which is evidently a global phenomenon.

The Ar/N, ratio of the air at La Jolla, California expressed as relative deviation from a reference. These data were obtained by using a continuous analyser (mass spectrometer) to directly analyze the air at La Jolla. Blue points: hourly Ar/N₂ data from La Jolla. Black curve: fit to semi-continuous data based on a two harmonic function and no trend. The Ar/N₂ ratio is potentially useful to trace largescale warming and cooling of the oceans. The Ar/N_{2} , ratio is higher in the summer than the winter due to warming of the surface ocean which drives outgassing of Ar due to the temperature dependence of the Ar solubility. The Ar release is offset by a small opposing N_2 release.

cords.

For more than decade, the program has been archiving CO₂ from air samples in sealed glass ampoules for retrospective analysis. As an example of an application, these archives have recently allowed the generation of time series of the radiocarbon ¹⁴C/¹²C content of atmospheric CO₂, which is relevant for assessing the distribution of carbon between reservoirs and the rates of fossil-fuel burning.

The O₂ program has also expanded recently to include measurements of the Ar concentration (as Ar/N_2 , ratio). This ratio varies as the ocean warms and cools due to thermally-driven ingassing and outgassing of Ar and N₂ by the oceans. The long-term trend in Ar concentration is expected to be useful for assessing the global ocean warming rate.

Forster, P. et al., 2007. Chapter 2: Changes in Atmospheric Constituents and in Radiative Forcing, Climate Change 2007, The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, pp. 129-234.

CO, EXTRACTION RACK

vstem for extracting CO₂ from flasks into glass ampoules. CO₂ is trapped cryogenically from the air using liquid nitrogen, and then transferred into a 1/4" O.D. glass tube. The tube is then ealed using an electronic heating element. Examples of the glass ampoules are shown in the insert. The system allows for up to six flask to be extracted in series. The archived samples have been used in support of ${}^{14}C/{}^{12}C$ analyses and for retrospective cross-checks on the calibration of ${}^{13}C/{}^{12}C$ and ${}^{18}O/{}^{16}O$ ratios.

GOALS & METHODS

Our measurements are pertinent to assessing global and hemispheric sources and sinks of CO₂ and their changes from year to year. The records are also relevant source/sink estimates on finer spatial scales, and are among the first places to look for evidence of climate feedbacks or other "surprises" in the re-

RECENT CONTRIBUTIONS

- Keeling, R.F., Manning, A.C., Paplawsky, W.J. and Cox, A.C., 2007. On the long-term stability of reference gases for atmospheric O_2/N_2 and CO2 measurements. Tellus 59B: 3-14.
- Rahmstorf, S., Cazenave, A., Church, J.A., Hansen, J.E., Keeling, R.F., Parker, D.E. and Somerville, R.C.J., 2007. Recent climate observations compared to projections. Science, 316(5825): 709-709.
- Manning, A.C. and Keeling, R.F., 2006. Global oceanic and land biotic carbon sinks from the Scripps atmospheric oxygen flask sampling network. Tellus, 58B: 95-116.
- Keeling, C.D., Piper, S.C., Bacastow, R.B., Wahlen, M., Whorf, T.P., Heimann, M. and Meijer, H.A., 2005. Atmospheric CO₂ and ¹³CO₂ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications. In: J.R. Ehleringer et al. (Ed.), A History of Atmospheric CO₂ and Its Effects on Plants, Animals and Ecosystems. Springer, pp. 83-113.

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