#### THE INCREASING CONCENTRATION OF ATMOSPHERIC CO<sub>2</sub>: HOW MUCH, WHEN, AND WHY?

Gregg Marland and Tom Boden Environmental Sciences Division Oak Ridge National Laboratory Oak Ridge, Tennessee 37831-6335, USA Phone 865-241-4850 Fax 865-574-2232 e-mail <u>gum@ornl.gov</u>

#### INTRODUCTION

There is now a sense that the world community has achieved a broad consensus that:

- 1.) the atmospheric concentration of carbon dioxide (CO<sub>2</sub>) is increasing,
- 2.) this increase is due largely to the combustion of fossil fuels, and
- 3.) this increase is likely to lead to changes in the global climate.

This consensus is sufficiently strong that virtually all countries are involved in trying to achieve a functioning agreement on how to confront, and mitigate, these changes in climate. This paper reviews the first two of these components in a quantitative way. We look at the data on the atmospheric concentration of carbon dioxide and on the magnitude of fossil-fuel combustion, and we examine the trends in both. We review the extent to which cause and effect can be demonstrated between the trends in fossil-fuel burning and the trends in atmospheric CO<sub>2</sub> concentration. Finally, we look at scenarios for the future use of fossil fuels and what these portend for the future of atmospheric chemistry. Along the way we examine how and where fossil fuels are used on the Earth and some of the issues that are raised by any effort to reduce fossil-fuel use.

#### **ATMOSPHERIC CO2**

Systematic monitoring of the atmospheric concentration of  $CO_2$  dates back to 1958 and the creation of the monitoring program at the Mauna Loa Observatory in Hawaii. This virtually continuous record now shows an increase from an average of 316.0 ppm (parts per million, by volume) in 1959 to 369.4 ppm in 2000 (Keeling and Whorf, 2001)(Figure 1). This increase represents an additional 114 x 10<sup>9</sup> metric tons of carbon in the atmosphere as  $CO_2$ . Analysis of proxy records, such as gas bubbles trapped in glacial ice, at a variety of places throughout the world suggests that the atmospheric concentration of  $CO_2$  has varied considerably over geologic time but generally remained in the range 280 +/- 10 ppm for several thousand years prior to the onset of the industrial era. Over the 420,000 years preceding the industrial era the concentration appears not to have exceeded 300 ppm (Barnola et al., 1999).

The atmospheric increase in CO<sub>2</sub> recorded at Mauna Loa is not unique to Mauna Loa but has been documented at many monitoring sites throughout the globe. An Italian monitoring site on Lampedusa Island, just south of Sicily, shows an increase from 360.8 ppm in 1993 to 371.3 ppm in 2000 (Chamard et al., 2001)(Figure 1), and the CDIAC data

files (<u>http://cdiac.esd.ornl.gov</u>) contain records from over 50 different sampling sites. It seems clear that the atmospheric concentration of  $CO_2$  is increasing and that it is now in a range that has not been experienced for perhaps 20 million years (IPCC, 2001).

#### FOSSIL FUEL COMBUSTION

Fossil fuels are burned in order to derive useful heat. Fossil-fuel burning involves the oxidation of hydrocarbon compounds and  $CO_2$  and  $H_2O$  are necessary and essential products. We can use the combustion of methane (CH<sub>4</sub>) to illustrate the reaction that takes place, and the essential difference for the other fossil fuels is their H to C ratio.

 $CH_4 + 2 O_2 = CO_2 + H_2O$ 

One consequence of the varying ratio of H to C is that different fuels have different rates of  $CO_2$  emissions per unit of useful energy (Table 1). For the basic fuel types there is a strong correlation between the C content and the energy content, so we can derive these coefficients that allow us to estimate  $CO_2$  emissions when fuel consumption is expressed in energy units.

Table 1: CO<sub>2</sub> Emission Rates for Fossil-Fuel Combustion (kg C /  $10^9$  joules gross heating value)

FUEL	CO <sub>2</sub> Emission Rate
Natural Gas	13.78
Petroleum	19.94
Hard Coal	24.15
Lignite and Brown Coal	25.22

#### **CO2 EMISSIONS FROM FOSSIL-FUEL COMBUSTION**

Total CO<sub>2</sub> emissions from fossil-fuel combustion for 1998 have been estimated at 6.4 x  $10^9$  metric tons of carbon, with another 0.2 x  $10^9$  tons C released during the calcining of limestone to make cement (Marland et al., 2001). This large and growing anthropogenic release of carbon to the atmosphere is a relatively recent phenomenon, having risen from a sum of 1.6 x  $10^9$  tons C in 1950. At the start of the  $20^{th}$  century it was  $0.5 \times 10^9$  tons C (see Figure 2). The fossil-fuel release occurs largely from energy consuming activities in the developed countries. North America and Western Europe contributed 38% of the total in 1998. That emissions growth is faster in the developing parts of the world is reflected in the fact that the contribution from North America and Western Europe was 71% of the total in 1950. Figures 3 and 4 show the history of emissions from major geographic regions. We show Germany as a separate region in order to preserve the discrete, historical representations of Eastern and Western Europe.

Given the apparently very large differences among emissions from various parts of the world, it is interesting to look at per capita emissions for some of the major countries. Figure 5 shows per capita emissions of  $CO_2$  from fossil-fuel burning and cement manufacture from the 20 countries with the largest total emissions in 1998. Per

capita emissions differ by greater than a factor of 10 from highly energy-intensive countries like the USA (5.4 t C/capita) to less energy-intensive countries like India (0.3 t C/capita)(Figure 5). At the global average,  $CO_2$  emissions amount to 1.13 tons C per capita.

In Tables 2 and 3 we contrast emissions data from 4 countries (USA, Italy, Norway, and China) to illustrate how the different countries and their varying economies and access to resources are reflected in their CO<sub>2</sub> emissions. Table 2 shows that per capita emissions from the USA are nearly 3 times those of the 2 European countries and 9 times those of China. Part of the differences among countries is seen in row 3 of the table, which reveals that China is the most dependent on coal while Norway derives a large fraction of its total energy supply from non-fossil sources. Row 4 of Table 2 gives insight into the structures and efficiencies of the economies. Countries with larger contributions from the primary and heavy, and hence energy-intensive, industries will have high emissions per unit of GDP while those in which the information and service industries play a larger role will have lower emissions per unit of GDP. Similarly an economy characterized by low efficiency will have higher C emissions per unit of GDP. Table 3 quickly reveals, for example, that electric power in Norway is largely non-fossil (e.g. hydro) and that the fossil-fuel based transportation system in China is much less developed than in the other countries.

	Italy	USA	Norway	China
Total emissions $(10^6 \text{ metric tons CO}_2)$	426	5410	34	2853
CO <sub>2</sub> /capita (t CO <sub>2</sub> /capita)	7.5	20.1	7.8	2.3
CO <sub>2</sub> /total primary energy supply (t CO <sub>2</sub> /Tj)	61	59	32	66
CO <sub>2</sub> /GDP (kg CO <sub>2</sub> /1999 US\$)	0.36	0.77	0.22	3.54

Table 2: CO<sub>2</sub> Emissions From Fossil-Fuel Burning (1998) (data from International Energy Agency, 2000)

Table 3: CO<sub>2</sub> Emissions by Sector (1998) (in percent, data from International Energy Agency, 2000)

	Italy	USA	Norway	China
Electric power (includes public heat)	31	44	1	40

Other energy industries	5	5	38	5
Manufacturing/Construction	19	10	21	33
Transport	26	30	36	8
Residential	16	6	3	7
Other	3	4	1	7

If we look at greenhouse gas emissions in the context of the Kyoto Protocol it is interesting to note that the Protocol makes no explicit acknowledgement of the many differences between countries that are reflected in the foregoing figures and tables. The Protocol does recognize the desire of developing countries to enjoy economic growth, and hence these countries have no commitments to limit emissions, and the negotiated targets do express minor differences in national commitments, as negotiated by the Parties largely on political grounds. Table 4 emphasizes that the Kyoto Protocol covers the full array of greenhouse gases (although CO<sub>2</sub> from the energy sector is the dominant greenhouse gas in all of the developed countries except New Zealand) and uses the USA as an example to show how the commitments are calculated. CO<sub>2</sub> is used as the reference and all gases are converted to "carbon equivalents" according to their integrated net impact on the global radiation balance over 100 years.

Greenhouse gas	Emissions in 1990 base	Computation for 2008 to 2012
	period	commitment period
CO <sub>2</sub>	1372	
CH <sub>4</sub>	179	
N <sub>2</sub> O	38	
HFCs/PFCs	19	
TOTAL, 1990	1608	
TARGET for 2008 to	7457	1608 x (1.00-0.07) x 5 = 1495 x 5
2012		

Table 4: USA Emissions Commitment From Kyoto (emissions in  $10^6$  tons carbon equivalent)

Collectively the Kyoto Protocol would, if it were to enter into effect, require that the 38 countries listed in its Annex B(developed countries and countries with economies in transition) reduce emissions for the period 2008 to 2012 to an average of 5.3% less than comparable emissions in 1990. Figure 6 shows how emissions from those countries listed in Annex B (and those countries not listed in Annex B) have progressed over the first 8 years following the reference year. Emissions from the Annex B have declined by 4% over the 8-year period while emissions from non-Annex B countries have increased by 30%. Severe economic problems in Eastern Europe have had a very large impact on the collective growth rate of emissions from the Annex B countries.

Before looking at the relationship between the atmospheric concentration of  $CO_2$  and emissions from fossil-fuel combustion, we note that  $CO_2$  has also been added to the atmosphere as a result of changes in land use and the destruction of terrestrial vegetation. Until the beginning of the 20<sup>th</sup> century emissions from land clearing were greater than those from fossil-fuel burning, but the latter now dominate by a factor of about 3 (Figure

7). Total emissions from 1850 to 1990 from land-use change amounted to about 124 x  $10^9$  t C.

#### ESTABLISHING CAUSE AND EFFECT

Returning to the atmosphere, we find that the cumulative total of  $CO_2$  emissions from fossil fuels (and cement manufacture) since the beginning of the industrial era have amounted to 270 x 10<sup>9</sup> t C (Figure 8). This anthropogenic emission to the atmosphere is about 45% of the pre-industrial atmosphere stock of  $CO_2$ , and the increase in atmospheric  $CO_2$  over this period represents about 42% of the fossil-fuel emissions. Over the decade of the 1990s the annual increase in the atmospheric concentration has ranged from 0.6 to 2.6 ppm, seemingly independent of the rate of releases from fossil fuels, and we have to ask whether the increase in atmospheric  $CO_2$  can be unambiguously attributed to releases from fossil fuels.

The global cycling of carbon involves complex interactions among the atmosphere, the oceans, the marine and terrestrial biospheres, volcanic eruptions, and rock weathering. Figure 9 provides a rough illustration of the major reservoirs and exchanges and shows that while anthropogenic, fossil-fuel emissions represent a sizeable perturbation on the system, some of the other stocks and flows are quite large by comparison.

Nonetheless, there are at least 4 lines of evidence that argue persuasively that it is the human perturbation, particularly the combustion of fossil-fuels that is driving the observed increase in atmospheric CO<sub>2</sub>. First, if we plot the cumulative increases in both atmospheric CO<sub>2</sub> and fossil-fuel emissions, we find that the two curves are tightly linked for the 40+ years of the Mauna Loa record. These cumulative curves smooth over the vear-to-vear variability in the functioning of the biosphere and the circulation of the ocean. Second, if we examine the latitudinal gradient of the concentration of atmospheric  $CO_2$ , as revealed in data from many monitoring sites, we observe that the concentration is growing more rapidly in the Northern Hemisphere, as expected with the fossil-fuel source some 95% in the Northern Hemisphere. Although CO<sub>2</sub> mixes throughout the atmosphere, there is a lag in the mixing between hemispheres that can be correlated with the latitudinal mix of sources and sinks. Third, the changing  ${}^{13}C/{}^{12}C$  ratio of atmospheric CO<sub>2</sub> tells something of the source of the excess C. Plants, and thus fossil fuels, preferentially concentrate the lighter <sup>12</sup>C. An increase in atmospheric CO<sub>2</sub> derived from burning fossil fuels or terrestrial vegetation should be accompanied by a decline in the  $^{13}C/^{12}C$  ratio whereas excess releases of CO<sub>2</sub> from the ocean or volcanoes, for example, would leave the atmospheric  ${}^{13}C/{}^{12}C$  ratio relatively unchanged. The observed changes in atmospheric  ${}^{13}C/{}^{12}C$  have been consistent with a CO<sub>2</sub> source from biologic materials. And, fourth, the declining concentration of atmospheric O<sub>2</sub> provides a compelling connection with increasing CO<sub>2</sub>. Only recently has it been possible to provide a sufficiently accurate record of atmospheric  $O_2$  to reveal that the increase in  $CO_2$  has been accompanied by the  $O_2$  decline that would be expected with a combustion source of  $CO_2$ (Keeling et al., 1996; Bender et al., 1998; Battle et al., 2000).

The evidence that increasing atmospheric  $CO_2$  is largely a consequence of fossil fuel burning seems very strong.

#### WHERE NOW?

Given the connection between atmospheric  $CO_2$  and fossil-fuel burning to date, it should be possible to model the future relationship. This does require a mathematical model that captures changes in ocean uptake, biologic responses, and concomitant changes in all portions of the global carbon cycle.

In 1992 the Intergovernmental Panel on Climate Change constructed and analyzed 6 scenarios, i.e. 6 possible paths for future emissions of greenhouse gases (see IPCC, 1995). Over the 6 scenarios  $CO_2$  emissions in the year 2100 ranged from 4.6 x 10<sup>9</sup> to 35.8 x 10<sup>9</sup> t C. The IPCC "business-a-usual" scenario (IS92a) suggested 2100 emissions at 20.3 x 10<sup>9</sup> t C. Using these emissions scenarios in several different models of the global carbon cycle, for the business-as-usual scenario the models suggested an atmospheric concentration approaching 700 ppm  $CO_2$  in 2100 (almost 2.5 times the pre-industrial concentration). Even for the lowest emitting IPCC scenario, in which emissions peak at 8.8 x 10<sup>9</sup> t C in 2025 before declining to 4.6 x 10<sup>9</sup> t C in 2100, the atmospheric concentration of  $CO_2$  continued to climb throughout the century, reaching a value near 480 ppm by 2100.

To see what it would take to get atmospheric  $CO_2$  to stabilize, Enting et al., 1994, conducted an interlaboratory model comparison exercise in which they 1.) described paths for the atmospheric concentration of  $CO_2$  stabilizing at various levels (at 350, 450, 550, 650, and 750 ppm), and 2.) asked scientists with mathematical models of the global carbon cycle to calculate what it would require in fossil-fuel emissions to get the atmospheric concentration to move along the prescribed paths to stable levels of  $CO_2$ . The results are shown in Figure 10. The conclusion is that if the atmospheric concentration of  $CO_2$  is to stabilize at a level even as high as 750 ppm, the path of emissions is probably going to have to diverge significantly from the business-as-usual path by the early decades of this century.

#### REFERENCES

Barnola, J.M., D. Raynaud, and C. Lorius, 1999. Historical CO<sub>2</sub> Record from the Vostok Ice Core, *in* Trends Online: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, at http://cdiac.esd.ornl.gov.

Battle, M., M. L. Bender, P. P. Tans, J. W. C. White, J. T. Ellis, T. Conway, and R. J. Francey, 2000. Global Carbon Sinks and Their Variability Inferred from Atmospheric  $O_2$  and del <sup>13</sup>C, Science 287: 2467-2470.

Bender, M. L., M. Battle, and R. F. Keeling, 1998. The O<sub>2</sub> Balance of the Atmosphere: A Tool for Studying the Fate of Fossil-Fuel CO<sub>2</sub>, Annual Reviews of Energy and Environment 23:207-223.

Chamard, P., L. Ciattaglia, L. di Sarra, F. Monteleone, 2001. Atmospheric Carbon Dioxide Record from Flask Measurements at Lampedusa Island, *in* Trends Online: A

Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, at http://cdiac.esd.ornl.gov.

Enting I. G., T. M. L. Wigley, and M. Heimann, 1994. Future Emissions and Concentrations of Carbon Dioxide: Key Ocean/Atmosphere/Land Analyses, Technical Paper No. 31, CSIRO Australlia, Canberra, 118 pp.

Houghton, R. A., and J. L. Hackler, 2001. Carbon Flux to the Atmosphere from Land-Use Changes: 1850-1990, *in* Trends Online: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, at http://cdiac.esd.ornl.gov.

IPCC, 1995. Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios, Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge UK.

IPCC, 2001. Climate Change 2001: the Scientific Basis, Summary for Policymakers and Technical Summary of the Working Group I Report, Intergovernmental Panel on Climate Change, Geneva, 98pp.

International Energy Agency, 2000. CO<sub>2</sub> Emissions from Fuel Combustion 1971-1998, OECD/IEA, Paris.

Keeling, R. F., S. C. Piper, and M. Heimann, 1996. Global and Hemispheric CO<sub>2</sub> Sinks Deduced from Changes in Atmospheric O<sub>2</sub> Concentration, Nature 381: 218-221.

Keeling, C. D., and T.P. Whorf, 2001. Atmospheric Carbon Dioxide Record from Mauna Loa, *in* Trends Online: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, at http://cdiac.esd.ornl.gov.

Marland, G., T. Boden, and R. J. Andres, 2001. Global, Regional, and National Annual CO<sub>2</sub> Emissions from Fossil-Fuel Burning, Cement Production, and Gas Flaring: 1751-1998, *in* Trends Online: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, at http://cdiac.esd.ornl.gov.

#### FIGURE CAPTIONS

Figure 1: The atmospheric concentration of CO<sub>2</sub> at Mauna Loa Observatory, Hawaii, and at Lampedusa Island, Italy.

Figure 2: Global total emissions of CO<sub>2</sub>, since 1950, from the combustion of fossil fuels and manufacture of cement.

Figure 3: Emissions of CO<sub>2</sub>, since 1950, from fossil-fuel combustion and cement manufacture in North America and Europe.

Figure 4: Emissions of  $CO_2$ , since 1950, from fossil-fuel combustion and cement manufacture in geographic regions other than North America and Europe. Figure 5: Total and per capita emissions of  $CO_2$ , for 1950 and 1958, for the 20 countries that had the largest total emissions in 1998.

Figure 6: CO<sub>2</sub> emissions, beginning in the 1990 base year, for those groups of countries that do (Annex B) and do not (non Annex B) have emissions limitations under the Kyoto Protocol. Emissions from fuels used in international commerce (bunker fuels) are shown with the country where the final fuel loading occurred, but these emissions would not be limited under the Protocol.

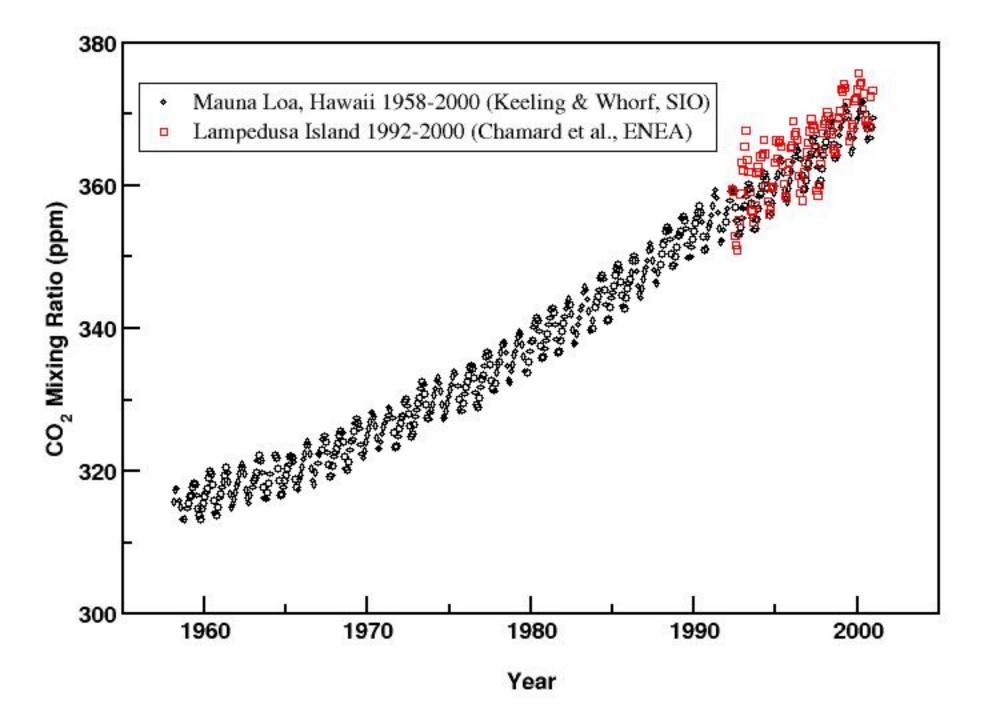
Figure 7: Emissions, by region, of  $CO_2$  from land-use change and the destruction of terrestrial vegetation. (Data are from Houghton and Hackler, 2001.)

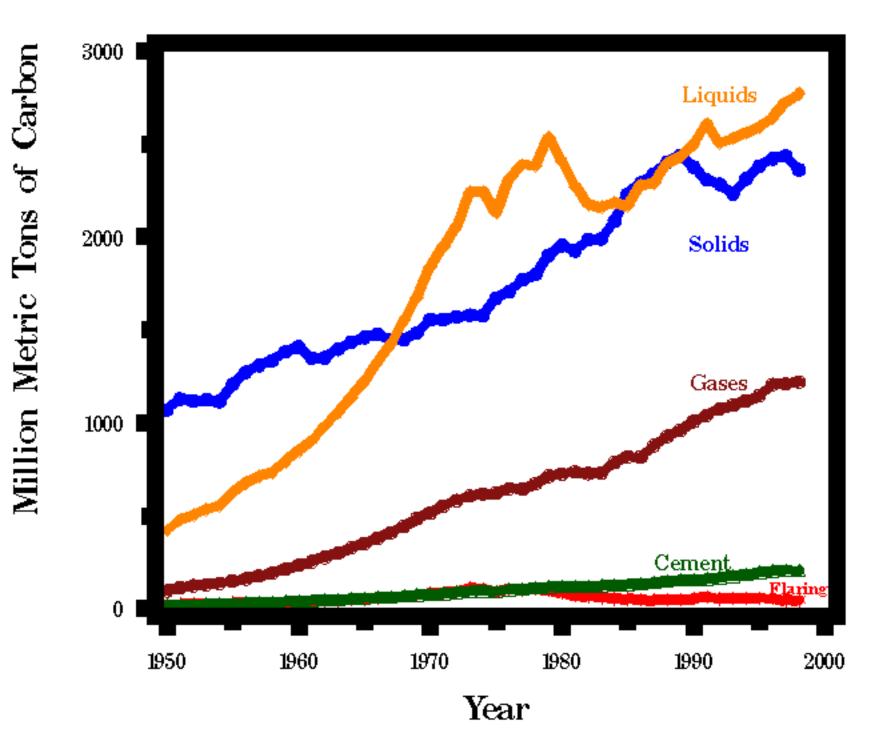
Figure 8: Cumulative emissions of CO<sub>2</sub> from fossil-fuel combustion and cement manufacture since the beginning of the fossil-fuel era.

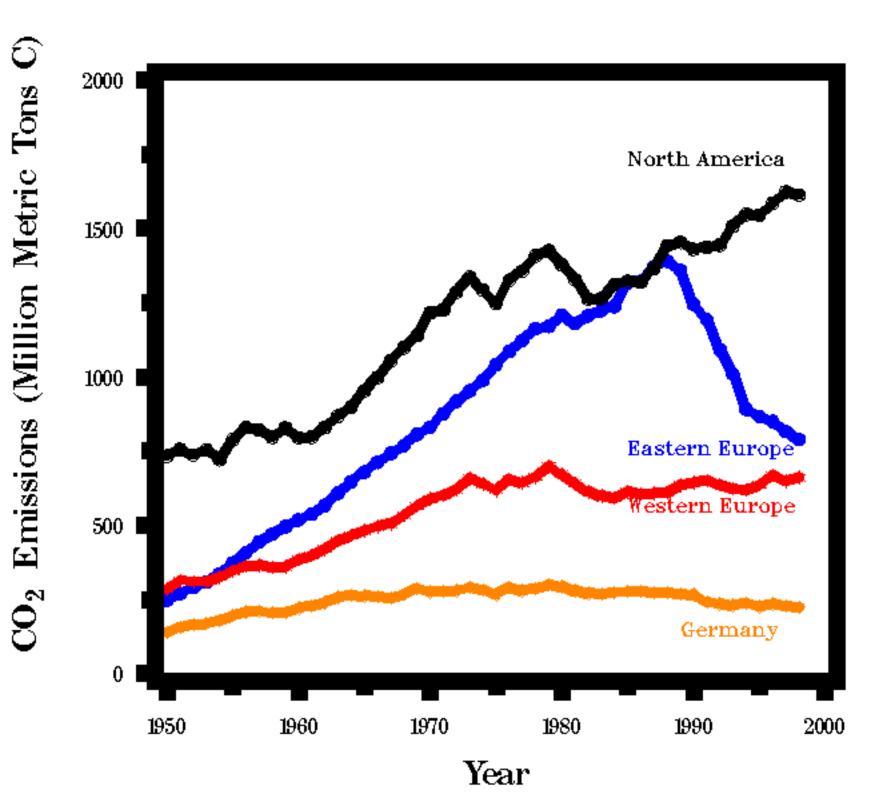
Figure 9: The major stocks and flows of the global carbon cycle.

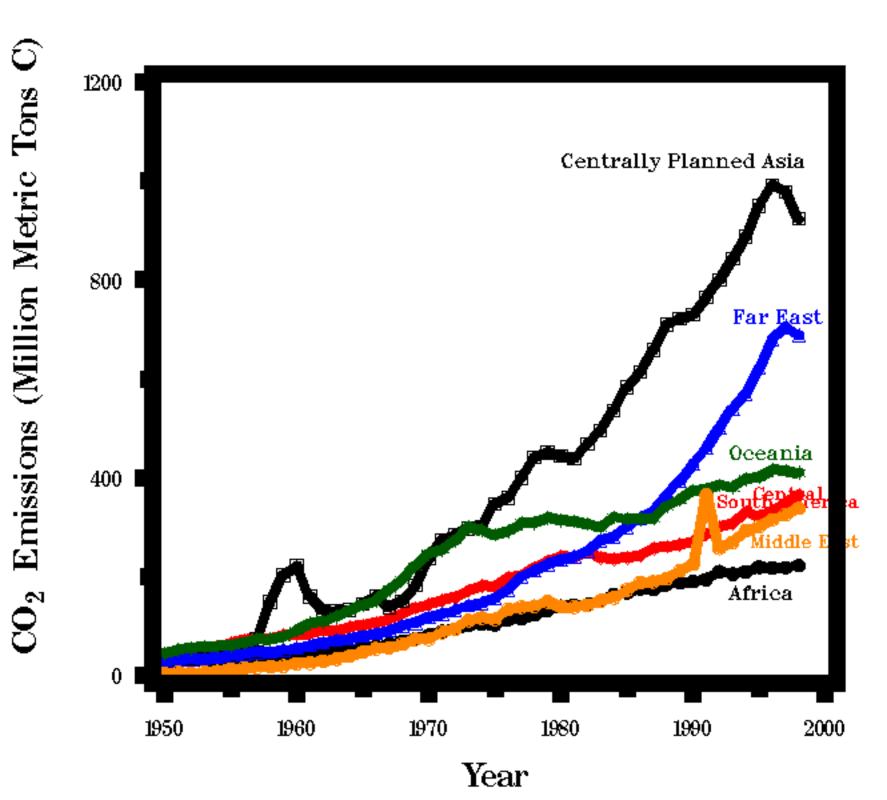
Figure 10: Computer model representations of the global carbon cycle. Curves show the emissions of  $CO_2$  from fossil-fuel burning that are consistent with prescribed paths for the eventual stabilization of the atmospheric concentration of  $CO_2$ . (from IPCC, 1995.) The numbers on the curves give the atmospheric concentration (in ppm) at which stabilization will eventually occur. Also shown are the paths of atmospheric  $CO_2$  for the high, low, and business-as-usual scenarios from the 1992 IPCC analyses (see IPCC, 1995).

## Atmospheric CO<sub>2</sub> Mixing Ratios: 1958-2000



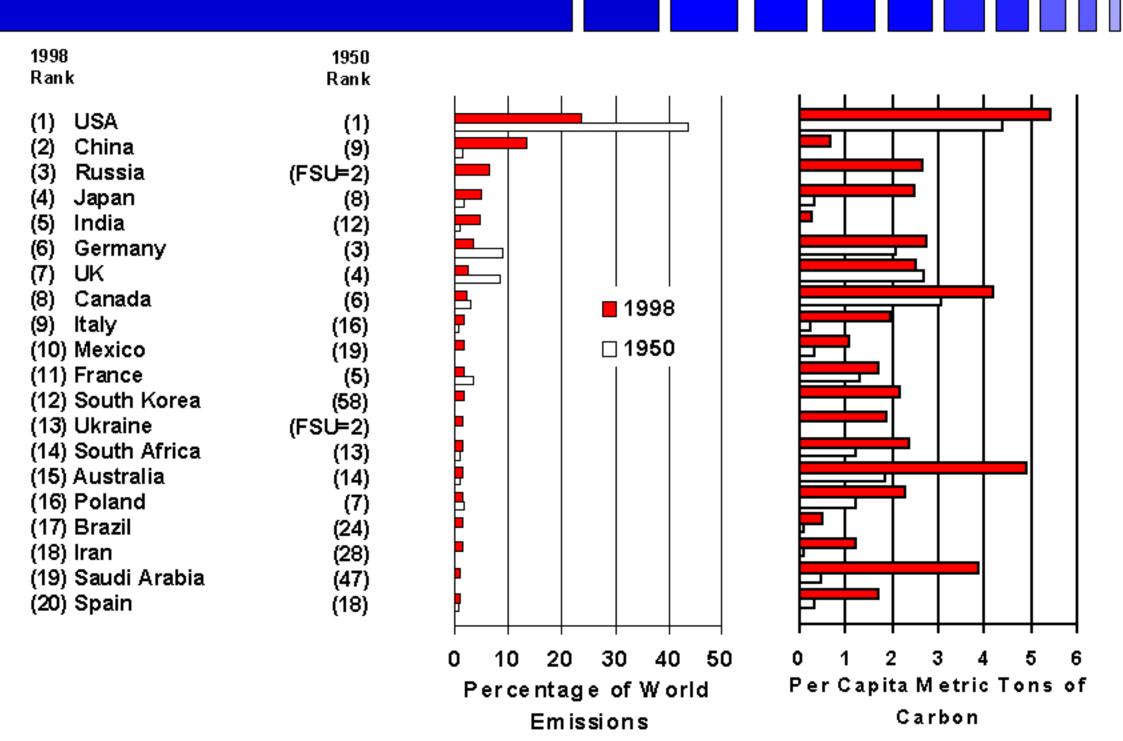








# Top 20 (1998 total CO<sub>2</sub> emissions)



#### Kyoto-Related Fossil-Fuel CO<sub>2</sub> Emission Totals

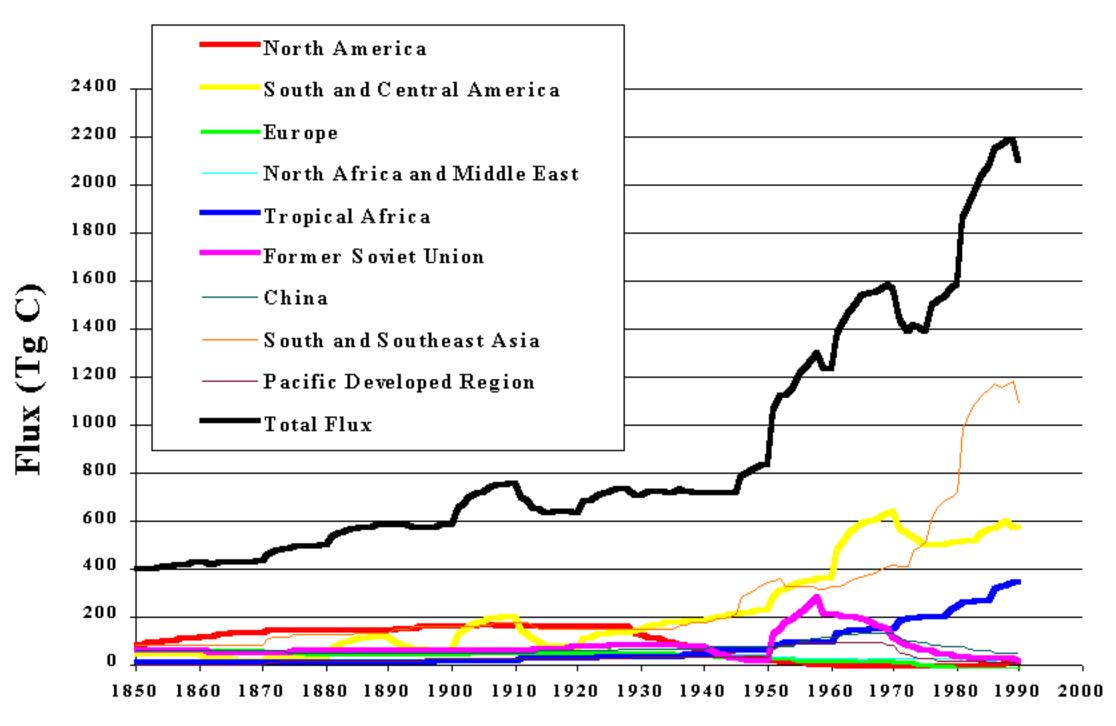
	Annex B C	ountries	Non Annex B Countries		
	<u>Fossil-Fuel CO2</u> <u>Emissions</u> (million metric tonnes C)	Bunkers (million metric tonnes C)	Fossil-Fuel CO <sub>2</sub> Emissions (million metric tonnes C)	Bunkers (million metric tonnes C)	
1990	3851	78	2126	41	
1991	3751	88	2306	41	
1992	3663	92	2291	43	
1993	3610	92	2341	48	
1994	3607	92	2487	50	
1995	3624	95	2607	52	
1996	3674	95	2704	58	
1997	3696	97	2775	61	
1998	3690	100	2756	62	

Source: Gregg Marland and Tom Boden (CDIAC, Oak Ridge National Laboratory).

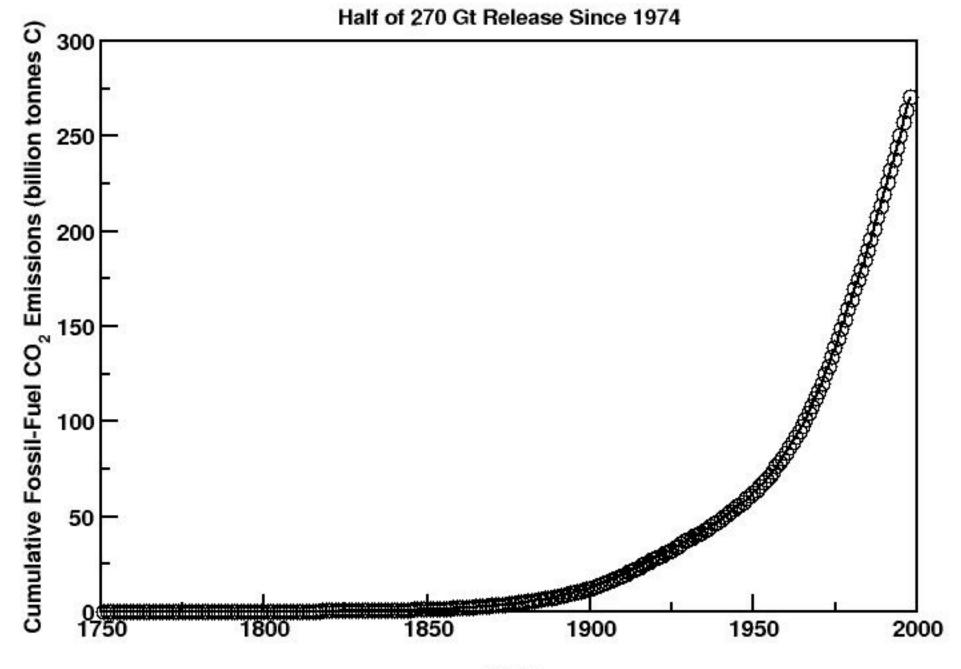
Table details provided as links.

Updated: 08/03/2001

### Annual Net Flux of Carbon to the Atmosphere from Land-Use Change: 1850-1990 (Houghton and Hackler)



Year

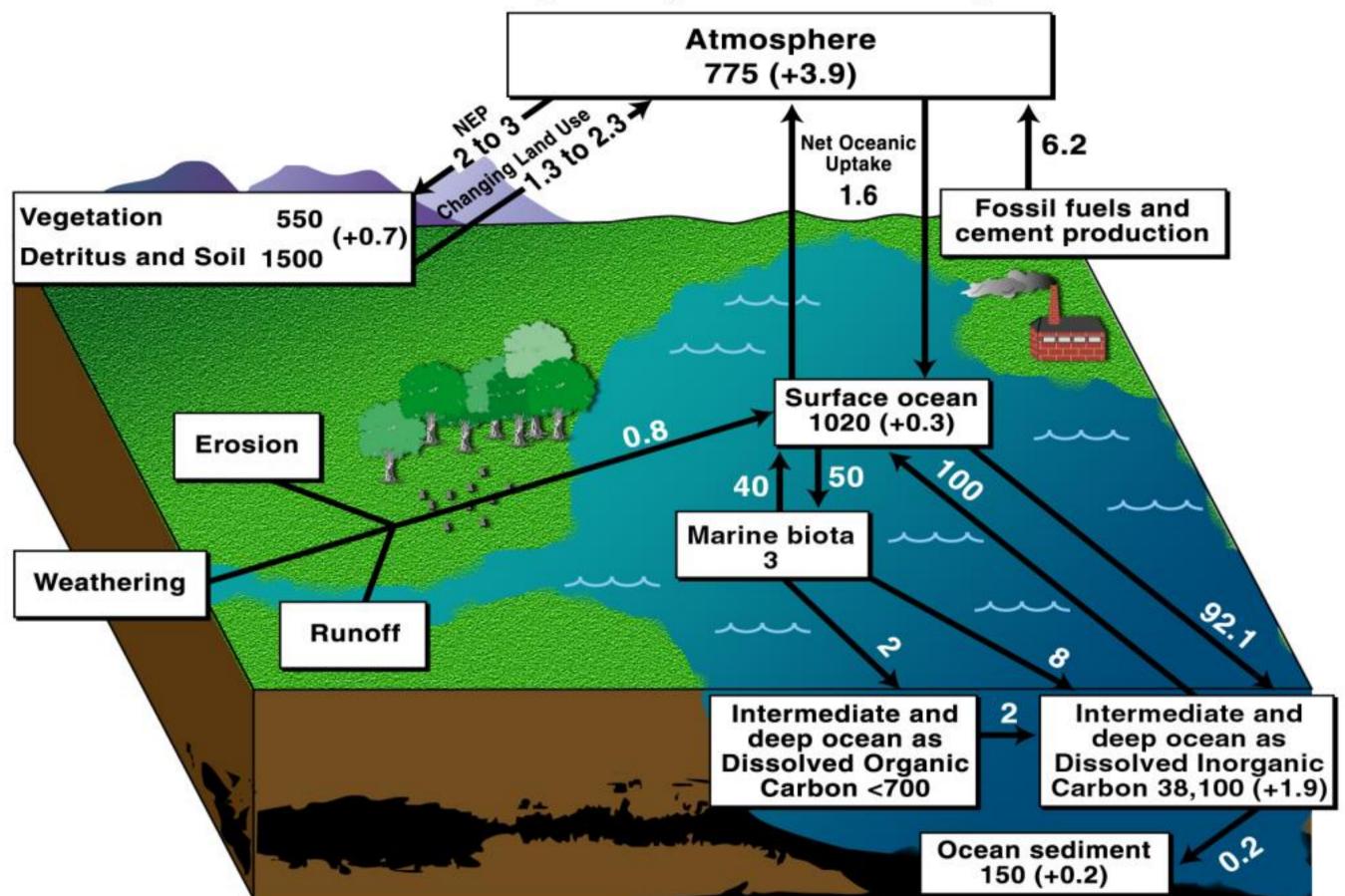


Cumulative Global CO<sub>2</sub> Emissions from Fossil-Fuel Consumption and Cement Production

Year

ORNL 2001-03372/gss

# Global Carbon Cycle (1992–1997)



The net terrestrial uptake estimate (0.7) considers gross primary production (~101.5), plant respiration (~50), decomposition (~50), and additional removal from the atmosphere directly or indirectly, through vegetation and soil, and eventual return to the ocean through the terrestrial processes of weathering, erosion and runoff (~0.8). Net oceanic uptake considers air/sea exchange (~90.8 gross release, ~92.4 gross uptake). All carbon reservoirs are expressed in Gt C (Gt C =  $10^{15}$  g C) with annual increments expressed in Gt C per year shown in parentheses. All fluxes are expressed in Gt C per year.



