

## Carbon Dioxide Emissions from Fossil Fuel Consumption and Cement Manufacture, 1751-1991; and an Estimate of Their Isotopic Composition and Latitudinal Distribution

Robert J. Andres, Gregg Marland, Tom Boden and Steve Bischof

Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6335 USA

### ABSTRACT

This work briefly discusses four of the current research emphases at Oak Ridge National Laboratory regarding the emission of carbon dioxide ( $\text{CO}_2$ ) from fossil fuel consumption, natural gas flaring and cement manufacture. These emphases include: 1) updating the 1950 to present time series of  $\text{CO}_2$  emissions from fossil fuel consumption and cement manufacture, 2) extending this time series back to 1751, 3) gridding the data at  $1^\circ$  by  $1^\circ$  resolution, and 4) estimating the isotopic signature of these emissions.

In 1991, global emissions of  $\text{CO}_2$  from fossil fuel and cement increased 1.5% over 1990 levels to  $6188 \times 10^6$  metric tonnes C. The Kuwaiti oil fires can account for all of the increase.

Recently published energy data (Etemad et al., 1991) allow extension of the  $\text{CO}_2$  emissions time series back to 1751. Preliminary examination shows good agreement with two other, but shorter, energy time series.

A latitudinal distribution of carbon emissions is being completed. A southward shift in the major mass of  $\text{CO}_2$  emissions is occurring from European-North American latitudes towards central-southeast Asian latitudes, reflecting the growth of population and industrialization at these lower latitudes.

The carbon isotopic signature of these emissions has been re-examined. The emissions of the last two decades are approximately 1‰ lighter than previously reported (Tans, 1981). This lightening of the emissions signature is due to fossil fuel gases and liquids, including a revision of their  $\delta^{13}\text{C}$  isotopic signature and an increased production rate.

### INTRODUCTION

Emissions of carbon dioxide ( $\text{CO}_2$ ) from the consumption of fossil fuels have resulted in an increasing concentration of  $\text{CO}_2$  in the atmosphere of the Earth. Combined with  $\text{CO}_2$  releases from changes in land use, these emissions have perturbed the natural cycling of carbon resulting in the accumulation of  $\text{CO}_2$  in the atmosphere and concern that this may significantly change the climate of the Earth (Houghton et al., 1992).

Understanding the changes now being observed and changes likely in the future requires the best possible information on the flows of carbon in the Earth system. Analyses summarized here are attempting to inventory the global magnitude and distribution of  $\text{CO}_2$  emissions from fossil fuel consumption. Recent interest in trying to limit the growth of atmospheric  $\text{CO}_2$  dictates understanding the sources of  $\text{CO}_2$  as a first step in trying to limit emissions. The 1992 Framework Convention on Climate Change,

DISTRIBUTION OF THIS DOCUMENT

MASTER

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

signed by 154 nations, requires that each nation conduct an inventory of the sources and sinks of greenhouse gases. This increasing concern and interest motivates the updating and improving of earlier CO<sub>2</sub> emission inventories (e.g. Keeling, 1973; Marland and Rotty, 1984; Marland et al., 1989; Marland and Boden, 1991; Marland and Boden, 1993).

International and national organizations have been systematically compiling statistics on world energy production and consumption since the early 1970's. These statistics are reported for individual countries and can be used with data on fuel chemistry and combustion characteristics to determine CO<sub>2</sub> emissions from fossil fuel consumption on national, regional and global scales. CO<sub>2</sub> emissions from cement manufacture contribute about 1 to 2% of that from fossil fuel production globally and are included here.

### THE 1950-1991 ANNUAL TIME SERIES

The 1950-1991 time series of CO<sub>2</sub> emissions from fossil fuel consumption and cement manufacture was calculated following the procedures in Marland and Rotty (1984) and Marland et al. (1989). Briefly, CO<sub>2</sub> emissions from fossil fuels are calculated from:

$$\text{CO}_{2,i} = \text{FP}_i \times \text{FO}_i \times \text{C}_i \quad (1)$$

where the three terms represent the net fuel production, the fraction of the fuel oxidized and the carbon content of the fuel, respectively, and *i* represents solid, liquid or gaseous fuels. Global totals of CO<sub>2</sub> emissions are calculated from national production data. National totals of CO<sub>2</sub> emissions are calculated from estimates of apparent consumption with FC<sub>*i*</sub> replacing FP<sub>*i*</sub> in (1) above, where FC<sub>*i*</sub> represents the national production data modified by national data on global trade and changes in stocks. The sum of FC<sub>*i*</sub> for all countries is less than the sum of FP<sub>*i*</sub> for all countries mainly because of the exclusion in national consumption data of bunker fuels, i.e. those fuels used for conducting international commerce; inaccuracies in reporting of imports and exports; and difficulty in accounting for non-fuel uses of fossil fuels, particularly the use of petroleum products in the chemical industry. Data on fuel production, trade and changes in stocks are obtained on magnetic media from the United Nations (U.N., 1993). Fuel oxidation and carbon content data come from a variety of sources as reported in Marland and Rotty (1984).

For cement manufacture, data are obtained from the United States Bureau of Mines (Solomon, 1993). An equation analogous to (1) is used to calculate CO<sub>2</sub> emissions from calcining CaCO<sub>3</sub>, with the cement chemistry data assembled by Griffin (1987).

The latest U.N. energy production data leads to a global CO<sub>2</sub> emission estimate of 6188 x 10<sup>6</sup> tonnes C for 1991 (Figure 1 and Table 1). This is about 1.5% more than the revised 1990 CO<sub>2</sub> emission estimate. It includes 123 x 10<sup>6</sup> metric tonnes C for oil combusted in the Kuwaiti oil field fires (estimation procedure described below). From 1990 to 1991, there was an increase in the apparent consumption of natural gas and in cement manufacture, but the global total of CO<sub>2</sub> would have shown a slight decline had

it not been for the Kuwaiti oil field fires.

With each annual release of the U.N. energy data, past data are also revised. The largest number of revisions occur in the first year after the initial release and the number of revisions drops considerably in subsequent years. Based on past years experience (Table 2), the 1991 number is likely within 2% of its final value. This is within the 10% error estimated for the global totals (see below).

An interesting facet of the 1991 results is the estimation of CO<sub>2</sub> emissions from Kuwait (Figure 2). The emissions from the oil fields being set ablaze were considerable and raise the issue of their proper allocation. The U.N. included in their energy statistics an estimate of the total gas flared from Kuwait in 1991 (Figure 2b). The total CO<sub>2</sub> emissions showed a decline in 1990 reflecting a decline in Kuwaiti energy production. However, in 1991, total emissions returned to a level indicative of the longer-term, steady growth in CO<sub>2</sub> emissions from Kuwait. But, this total emission curve is strongly affected by the gas flaring resulting from the oil fields being set ablaze.

Figure 2a is a more realistic picture of Kuwaiti CO<sub>2</sub> emissions resulting from their energy production. It differs from Figure 2b in that the 1991 emissions from gas flaring (8.1 million metric tonnes C) have been reduced by 90%. This reduction is based on a U.N. estimate that only 10% of the gas flaring resulted from normal oil field production procedures and the other 90% from the oil field fires (S. Hussein, U.N. Energy Statistics Office, personal communication, 1993). Ferek et al. (1992) estimated that 7% of the carbon discharged from the oil field fires during May and June 1991 was from burning of natural gas rather than oil. Combined with our estimate of oil burning (below), this implies that 8.6 million metric tonnes C were discharged from natural gas burning and this agrees well with the estimate based on U.N. (1993) energy data. The differences in Figures 2a and 2b are limited to the year 1991 and are not major. They suggest that CO<sub>2</sub> emissions from oil-field-fire gas flaring could be allocated to Kuwait without significantly changing the long-term emissions pattern of Kuwait.

However, if CO<sub>2</sub> emissions from oil-field-fire gas flaring are allocated to Kuwait, should not the CO<sub>2</sub> emissions from oil-field-fire oil burning also be allocated to Kuwait (Figure 2c)? The U.N. (1993) energy data do not include oil lost during the fires. By using detailed tables of average flow rate per week for the interval from March 16 until the last fires were extinguished on November 6 (the first fires were ignited in late January, but the first one extinguished was on March 23) (NOAA, 1991), the amount of oil released in the fires is estimated at 1060 million barrels combusted and another 60 million barrels spilled, but not combusted. Of the spilled oil, some small fraction was recovered and the rest either seeped into the ground or was covered with sand. Based on measurements made in the plume during May and June 1991, 96% of the fuel carbon emitted was as CO<sub>2</sub> while only 0.53% was as soot (Ferek et al., 1992; Laursen et al., 1992). Carbon was also discharged as CO, CH<sub>4</sub>, and other organic volatiles and particulates. Because much of this carbon is soon converted to CO<sub>2</sub> in the atmosphere, approximately 99% of the fuel carbon ended up in the atmosphere as CO<sub>2</sub>. Given an oil density of 0.86 kg/l and a carbon content of 85% (Laursen et al., 1992), the total CO<sub>2</sub> discharged contained about 123 million tonnes C.

Figure 2c is the same as Figure 2b, but includes the CO<sub>2</sub> emissions from the oil

combusted during the 1991 oil field fires. The inclusion of this source dwarfs the other emissions from Kuwait. In a global context, this source is greater than the increase in total CO<sub>2</sub> emissions from 1990 to 1991. Without including the CO<sub>2</sub> emissions released from the oil field fires (liquids and gas flaring) in Kuwait, the 1991 CO<sub>2</sub> emissions estimate for Kuwait is only 99.3% of the revised 1990 estimate.

Because of unique situations, such as the oil field fires, and a basic data set which is annually updated, the global CO<sub>2</sub> calculations are periodically revised. Ongoing work with global CO<sub>2</sub> calculations currently includes refining the supporting data used to calculate emissions from the U.N. energy data. This includes the acquisition of new data on the carbon content of fossil fuels, especially solids, and efforts to refine estimates of the geographic distribution of emissions on a 1° x 1° global grid. The gridded data is part of the Global Emissions Inventory Activity, an activity of the International Global Atmospheric Chemistry Project of the International Geosphere-Biosphere Programme. Included in the refinement will also be a reexamination of the higher and lower heating values of fossil fuels and the role they have played in past calculations. Finally, the re-evaluation of the slow oxidation of fossil fuels used in non-fuel uses will be included in future work.

Marland and Rotty (1984) estimated that the uncertainty in the global total CO<sub>2</sub> emissions estimates was 6 to 10% and, acknowledging the subjectivity involved in those estimates, those estimates have not been reevaluated. While ongoing work can provide refinements in the chemistry and the fate of fuels and fuel products, the major source of uncertainty is in the national statistics on fuel production and trade. These statistics vary in quality among countries and international statistical offices like that in the U.N. are obligated to rely on data they can obtain from national sources or energy industries.

A recent assessment conducted by the Energy Information Administration (EIA) of the U.S. Department of Energy provides an insight into the uncertainty of national data by looking at some of the supporting data used to generate their own estimates (EIA, 1989). Data on the quantities of fuel received and consumed by electric utilities in the U.S. would be expected to be among the best energy data available. The EIA compared data on fuel receipts at electric utilities, compiled from one questionnaire, against data on fuel consumption plus changes in stocks, compiled from another questionnaire. Both questionnaires were completed by the utilities themselves. Receipts should equal consumption plus the change in stocks. With focused inquiry, the EIA was able to offer a variety of reasons why the equality might not hold (including different sampling strategies between the two forms, reporting lags between the two forms, loss of coal from stockpiles by wind and oxidation, etc.), but it is interesting to see the magnitude of the difference between two numbers which one expects to be equal. For coal, receipts and consumption plus changes in stock were within 3% for all 10 U.S. census regions and the national totals differed by less than 0.8%. For petroleum and natural gas, the difference exceeded 5% in several census regions and the national totals differed by about 1.3% for petroleum and about 6.3% for natural gas.

With increasing interest in greenhouse gas emissions and the number of people making greenhouse gas emissions estimates, the data presented here will provide opportunity for comparisons with other estimates. Some of these estimates will rely on

the same U.N. energy data, but others will be based on national energy data that may not be broadly available. The most comprehensive set of alternate, CO<sub>2</sub> emissions calculations presently available are those compiled by Susan Subak and her colleagues at the Stockholm Environment Institute (von Hippel et al., 1993). They calculated CO<sub>2</sub> emissions for 1988 based on energy data from the IEA/OECD when possible and the U.N. when necessary. Their global total differs from that presented here by less than 2.1% although there is a striking difference in some of the national totals. Because their treatment of the national, apparent-consumption, energy data is slightly different, direct comparison between the two studies is difficult and requires caution.

## A 1751-1991 TIME SERIES

Etemad et al. (1991) recently published a volume on world energy production at varying temporal resolutions from 1800 to 1985. Footnotes in the text extend production data back to 1751. These data can be treated in the same manner as the U.N. energy data to obtain a time series of CO<sub>2</sub> emissions from fossil fuel production.

Preliminary analysis shows good agreement between this time series and others currently available (Table 3). In comparison to the estimates of CO<sub>2</sub> emissions from 1860 to 1953 compiled by Keeling (1973), calculations based on the Etemad et al. (1991) data are always within 5%, usually within 3%. Similar agreement is found between CO<sub>2</sub> estimates based on the Etemad et al. (1991) data and on the 1950-1991 U.N. (1993) data. For the four years of overlap between Keeling (1973) and the calculations based on U.N. (1993) energy data, the agreement is within 1%.

A preliminary time series of cumulative CO<sub>2</sub> emissions since 1751, whose values may change slightly as the full energy set becomes available, is presented in Figure 3 and Table 4. For 1751-1949, the time series is based on calculations using summary data for a limited number of years (Etemad et al., 1991) with extrapolation between those years. For 1950-1991, the time series is based on calculations using the U.N. (1993) energy data.

The time series shows over two million metric tonnes of carbon had already been released to the atmosphere by 1751. Cumulative emissions topped 100 million metric tonnes C by 1781, and over 1 billion metric tonnes C had been released to the atmosphere by the mid-1840's.

Further refinement of the pre-1950 part of the time series depends on a fuller analysis of the Etemad et al. (1991) data. This requires access to supporting data not published in the book. This supporting data is currently being sought. Completion of the ongoing analysis of this data set will supply a better time series of fossil fuel CO<sub>2</sub> emissions to the atmosphere back to 1751. This will complement carbon cycle modelling studies which often begin their analyses in the early 1700's.

## THE LATITUDINAL DISTRIBUTION

A data set of CO<sub>2</sub> emissions on a uniform geographic basis can be constructed from the country CO<sub>2</sub> emissions data. The challenge is to allocate emissions within countries based on either sub-country data on energy use or on proxy data like

population density. The current effort to distribute CO<sub>2</sub> emissions from fossil fuels on a 1° latitude by 1° longitude grid updates the 5° x 5° grid used by Marland et al. (1985). The 360 longitudinal grid spaces in each latitudinal band can be summed to determine the latitudinal emissions.

A sense of the latitudinal changes which are occurring can be gained from the within-country, energy-consumption distributions estimated for 1980 (Marland et al., 1985) and national fossil fuel CO<sub>2</sub> emissions calculated with 1989 energy use data (Marland and Boden, 1989) (Figure 4). The bulk of fossil fuel CO<sub>2</sub> emissions is shifting southward with increasing global industrialization.

## THE ISOTOPIC SIGNATURE

The carbon isotopic ( $\delta^{13}\text{C}$ , PDB) signature of fossil fuel emissions has decreased during the last century, reflecting the changing mix of fossil fuels produced. Previous estimates of  $\delta^{13}\text{C}$  of anthropogenic CO<sub>2</sub> emissions have assumed an average world wide value for each fuel type that is invariant with time and area of production (Tans, 1981). Combining updated  $\delta^{13}\text{C}$  signatures with the anthropogenic CO<sub>2</sub> emissions estimates, allows a new estimate of global, average  $\delta^{13}\text{C}$  signature which considers emissions type and geographic origin. The improved fossil fuel  $\delta^{13}\text{C}$  signature should provide an additional constraint for balancing the sources and sinks of the global carbon cycle.

The variability in the  $\delta^{13}\text{C}$  values of coals is small and thus the average isotopic ratio of -24.1‰ adopted by Tans (1981) is within  $\pm 0.3\%$ , regardless of source. Over 80% of coal is composed of humic materials or type III kerogen which shows little variability in isotopic composition (Redding et al., 1980). Even after significant thermal alteration, coal retains the isotopic signature of its source material to within  $\pm 0.3\%$  (Craig, 1953; Jeffrey et al., 1955). It is the relatively unchanged isotopic composition of the humic materials and kerogen which determines the isotopic signature of coals.

Oil shows a significant spread of  $\delta^{13}\text{C}$  isotopic values, from -19‰ to -35‰. The modal value of  $\delta^{13}\text{C}$  of oil is near -26.5‰ (Degens, 1967). However, this modal value does not represent the average value of oil produced for energy. The average value for the oil consumed must be weighted by the production from various oil producing regions since different regions often have characteristic  $\delta^{13}\text{C}$ .

Several important oil producing regions during the last two decades have  $\delta^{13}\text{C}$  values near -30‰ or lighter. These areas include the North Slope of Alaska, the North Sea, the Western Siberian Basin and the large non-marine basins in China. The individual isotopic values for oil production in the top 17 oil producing countries have been taken from the published literature (Galimov, 1973; Yeh and Epstein, 1981; Wanli, 1985; Golyshev et al., 1991; Chung et al., 1992; Philp et al., 1992; and references contained therein). For minor petroleum producing countries the modal value of -26.5‰ is used (Degens, 1967; Tans, 1981). In the U.S.A., the shift in production from isotopically heavy California oil to isotopically light Alaskan oil has shifted the oil-production-weighted  $\delta^{13}\text{C}$  value from approximately -26.5‰ in 1950 to -27.5‰ in 1991. A similar shift, from approximately -28‰ in 1965 to -30‰ in 1980, has occurred in the former U.S.S.R., as production shifted during the late 1960's and 1970's from the Caspian and



Volga-Ural regions to the fields in western Siberia (Riva, 1991). Between 1950 and 1990 the global, oil-production-weighted  $\delta^{13}\text{C}$  signature decreased by 1.3‰, from -26.5‰ to -27.8‰.

Natural gas shows the greatest variability in  $\delta^{13}\text{C}$  of any natural substance (Schoell, 1988). Methane associated with coal may be as heavy as -20‰, while methane from marine sediments may be lighter than -100‰ (Schoell, 1988). Natural gas produced for fuel can be divided into separate genetic groups, thermogenic and biogenic gases, with different  $\delta^{13}\text{C}$  isotopic signatures (Schoell, 1984). Since 80% of the gas production of the world is thermogenic (Rice and Claypool, 1981), a weighted average of 193 thermogenic (-40‰) and 55 biogenic (-65‰) methane gases would have a mean of -45‰. However, natural gas also contains  $\text{C}_2$  and  $\text{C}_3$  gases which are often 10‰ to 20‰ heavier than methane, but are rarely more than 10% of natural gas. This results in an average  $\delta^{13}\text{C}$  of about -44‰ for natural gases.

While it would be appropriate to weight the values for natural gas production by source within each region of production or country, the variability of  $\delta^{13}\text{C}$  values of natural gases, even within a single field, make it difficult to estimate a weighted-average value. An example is the Anadarko Basin, a major natural gas production zone in the U.S.A., which has  $\delta^{13}\text{C}$  ranging from -33.2‰ to -49.8‰, with a mean value near -43.5‰ (Rice et al., 1988). The world average of -44.0‰ may be a heavy estimate when natural gas production in the former U.S.S.R. is considered. The U.N. energy data show that the former U.S.S.R. produced 32% of the world's total natural gas production in 1990. Much of this production was concentrated in the gas fields of western Siberia, which is characterized by  $\delta^{13}\text{C}$  of -46‰ to -50‰ and hydrocarbon composition of greater than 99% methane (Galimov, 1988). Because of the variability in  $\delta^{13}\text{C}$  isotopic signature and lack of sufficient field production data, the average  $\delta^{13}\text{C}$  of -44‰ calculated above is used for all natural gas production.

Methane associated with liquid petroleum has an average value near -40‰ (this study, calculated thermogenic average). Thus, this is the  $\delta^{13}\text{C}$  isotopic signature used for gas flaring.

As is the case for coal, the variability in the  $\delta^{13}\text{C}$  values of cement is small and the 0‰ average isotopic ratio adopted by Tans (1981) is within  $\pm 0.3$ ‰. Limestones, the source material for cement, have a mean isotopic value around 0‰, which reflects the equilibrium value with the ocean at the time of formation (Garrels and Mackenzie, 1971). The calcite in limestones may undergo diagenesis, which can change the  $\delta^{13}\text{C}$  value toward lighter values. However, most limestones used for cement manufacture are considered unaltered, and retain a value near 0‰.

The  $\delta^{13}\text{C}$  value of total  $\text{CO}_2$  emitted from anthropogenic sources was calculated by using the production of carbon for each fuel type by country and multiplying it by the appropriate  $\delta^{13}\text{C}$  value. A value of -24.1‰ for coal, -44‰ for natural gas, -40‰ for gas flaring and 0‰ for cement production were used for all countries and all years. Fifteen of the top oil producing countries were assigned unique isotopic values for oil production that did not vary with time. In addition, for the U.S.A. and the former U.S.S.R, isotopic values for oil production changed with time as the location of production fields changed. The  $\delta^{13}\text{C}$  used for U.S.A. oil decreased linearly between 1950 and 1991, while the  $\delta^{13}\text{C}$

used for former U.S.S.R. oil decreased in two linear steps: 1965 to 1975 and 1975 to 1980. For all remaining countries, the modal value for oil, -26.5‰, was used. Using these  $\delta^{13}\text{C}$  isotopic signatures (Table 5) and the national  $\text{CO}_2$  emissions data calculated from (1) above, the  $\delta^{13}\text{C}$  value of  $\text{CO}_2$  produced for each year from fossil fuels and cement was calculated (Figure 5 and Table 1). The absolute accuracy for the method of calculating the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  emissions from fossil fuel production and cement manufacture is approximately  $\pm 0.5\%$ . Table 1 shows  $\delta^{13}\text{C}$  with two decimal places so that the relative structure of the time series can be seen.

## EPILOGUE

The estimation of  $\text{CO}_2$  emissions from fossil fuel consumption and cement manufacture is fundamental to understanding the human perturbation of the global carbon cycle. The better the magnitude, distribution and  $\delta^{13}\text{C}$  isotopic signature are known, the better our chance to understand the functioning of the global carbon cycle now and changes which are to be anticipated in the future.

As the tide grows for controlling global  $\text{CO}_2$  emissions, national and regional political bodies are searching for means to reduce or offset the impact of the emissions originating from within their jurisdictions. Calculations of greenhouse gas emissions are now taking place in many national and international groups. The annual data set on  $\text{CO}_2$  emissions from fossil fuel consumption and cement manufacture is intended to provide a well-documented, technically sound data set of  $\text{CO}_2$  emissions for use by the scientific community and a bench mark for the policy community. It is periodically revised as new data become available. This partially results from increased international interest which improves the national data sets of energy production and consumption on which these  $\text{CO}_2$  emission estimates rely.

**ACKNOWLEDGEMENTS.** RJA is supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute for Science and Education (ORISE). GM and TB are supported by the Global Change Research Program, Environmental Sciences Division, Office of Health and Environmental Research, DOE, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. SB is supported by a Graduate Fellowship for Global Change, sponsored by DOE, administered by ORISE.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

## REFERENCES

- Chung, H.M., M.A. Rooney, M.B. Toon, and G.E. Claypool. 1992. Carbon isotope composition of marine crude oils. Bulletin of the American Association of Petroleum Geologists 76, 1000-1007.
- Craig, H. 1953. The geochemistry of stable carbon isotopes. Geochimica et Cosmochimica Acta 3, 53-92.
- Degens, E.T. 1967. Biogeochemistry of Stable Carbon Isotopes. In Organic Geochemistry: Methods and Results (G. Elginton and M.T.J. Murphy, eds.), Springer-Verlag, New York, 304-329.
- EIA. 1989. An Assessment of the Quality of Selected EIA Data Series. DOE/EIA-0292(87), Energy Information Administration, Department of Energy, Washington, DC, 68 pp.
- Etemad, B., J. Luciani, P. Bairoch, and J.-C. Toutain. 1991. World Energy Production: 1800-1985. Librairie DROZ, Geneva, 272 pp.
- Ferek, R.J., P.V. Hobbs, J.A. Herring, K.K. Laursen, R.E. Weiss, and R.A. Rasmussen. 1992. Chemical composition of emissions from the Kuwait oil fires. Journal of Geophysical Research 97, 14483-14489.
- Galimov, E.M. 1973. Isotopy ugleroda v neftegazovoy geologii. Nedra, Moscow, 384pp. [English translation: Galimov, E.M. 1975. Carbon Isotopes in Oil and Gas Geology. NASA, Washington DC, TT 682, 387 pp.
- Galimov, E.M. 1988. Sources and mechanisms of formation of gaseous hydrocarbons in sedimentary rocks. Chemical Geology 71, 77-95.
- Garrels, R.M., and F.T. Mackenzie. 1971. Evolution of Sedimentary Rocks. Norton and Co., New York, 397 pp.
- Golyshev, S.I., N.A. Verkhovskaya, and V.A. Burkova. 1991. Stable carbon isotopes in source-bed organic matter of West and East Siberia. Organic Geochemistry 17, 277-291.
- Griffin, R.C. 1987. CO<sub>2</sub> Release from Cement Production 1950-1985. Institute for Energy Analysis, Oak Ridge Associated Universities, Oak Ridge, Tennessee, 30 pp.
- Houghton, J.T., B.A. Callender, and S.K. Varney (eds.). 1992. Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment. Intergovernmental Panel on Climate Change, WMO/UNEP, University Press, Cambridge, U.K., 200 pp.
- Jeffrey, P.M., W. Compston, D. Greenhalgh, and B.C. Heezen. 1955. On the carbon-13 abundance of limestones and coals. Geochimica et Cosmochimica Acta 7, 255-286.
- Keeling, C.D. 1973. Industrial production of carbon dioxide from fossil fuels and limestone. Tellus 2, 174-198.
- Laursen, K.K., R.J. Ferek, P.V. Hobbs, and R.A. Rasmussen. 1992. Emission factors for particles, elemental carbon, and trace gases from the Kuwait oil fires. Journal of Geophysical Research 97, 14491-14497.
- Marland, G. 1990. CO<sub>2</sub> emissions - modern record. In TRENDS '90: A Compendium of Data on Global Change (T.A. Boden, P. Kanciruk, and M.P. Farrell, eds.). ORNL/CDIAC-36, Carbon Dioxide Information Analysis Center, Oak

- Ridge National Laboratory, Oak Ridge, Tennessee, 92-133.
- Marland, G., and T.A. Boden. 1989. Carbon dioxide releases from fossil-fuel burning, testimony before the Senate Committee on energy and natural resources, 26 July 1989. Senate Hearing 101-235. DOE's National Energy Plan and Global Warming, U.S. Senate, U.S. Government Printing Office, Washington, DC, 62-84.
- Marland, G., and T.A. Boden. 1991. CO<sub>2</sub> emissions - modern record. In Trends '91: A Compendium of Data on Global Change (T.A. Boden, R.J. Sepanski, and F.W. Stoss, eds.). ORNL/CDIAC-46, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 386-507.
- Marland, G., and T. Boden. 1993. The magnitude and distribution of fossil-fuel-related carbon releases. In The Global Carbon Cycle (M. Heimann, ed.), NATO Advanced Study Institute, il Ciocco, Italy, Springer-Verlag, New York, 117-139.
- Marland, G., T.A. Boden, R.C. Griffin, S.F. Huang, P. Kanciruk, and T.R. Nelson. 1989. Estimates of CO<sub>2</sub> Emissions from Fossil Fuel Burning and Cement Manufacturing, Based on the United Nations Energy Statistics and the U.S. Bureau of Mines Cement Manufacturing Data. NDP-030, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 712 pp.
- Marland, G., and R.M. Rotty. 1984. Carbon dioxide emissions from fossil fuels: A procedure for estimation and results for 1950-1982. Tellus 36B, 232-261.
- Marland, G., R.M. Rotty, and N.L. Treat. 1985. CO<sub>2</sub> from fossil fuel burning: Global distribution of emissions. Tellus 37B, 243-258.
- National Oceanic and Atmospheric Administration. 1991. Kuwait Oil Fire Extinguishing Chronology. Office of the Chief Scientist, Gulf Program Office, U.S. Department of Commerce. Washington, DC, 38 pp.
- Philp, R.P., J.H. Chen, J.M. Fu, and G.Y. Sheng. 1992. A geochemical investigation of crude oils and source rocks from Biyang Basin, China. Organic Geochemistry 18, 933-945.
- Redding, C.E., M. Schoell, J.C. Monin, and B. Durand. 1980. Hydrogen and carbon isotopic composition of coals and kerogen. In Advances in Organic Geochemistry (A.G. Douglas and J.R. Maxwell, eds.), Pergamon, Oxford, 711-723.
- Rice, D.D., and G.E. Claypool. 1981. Generation, Accumulation and Resource Potential of Biogenic Gas. Bulletin of the American Association of Petroleum Geologists 65, 5-25.
- Rice, D.D., C.N. Threlkeld, and A.K. Vuletich. 1988. Character, origin and occurrence of natural gases in the Anadarko Basin, southwestern Kansas, western Oklahoma and Texas Panhandle, U.S.A. Chemical Geology 71, 149-157.
- Riva, Jr., J.P. 1991. Soviets may halt production drop with outside funds, technologies. Oil and Gas Journal 89, 110-112.
- Schoell, M. 1984. Wasserstoff- und Kohlenstoffisotope in organische Substanzen, Erdolen, und Erdgasen. Geologisches Jahrbuch, Riehe D 67, 1-164.
- Schoell, M. 1988. Multiple origins of methane in the earth. Chemical Geology 71, 1-10.
- Solomon, C. 1993. Cement. U.S. Department of Interior, Bureau of Mines, 25 pp.
- Tans, P. 1981. 13C/12C of industrial CO<sub>2</sub>. In SCOPE 16: Carbon Cycle Modelling (B. Bolin, ed.), John Wiley and Sons, Chichester, England, 127-129.

- U.N. 1993. The United Nations Energy Statistics Database. United Nations Statistical Division, New York.
- von Hippel, D., P. Raskin, S. Subak, and D. Stavisky. 1993. Estimating greenhouse gas emissions from fossil fuel consumption: Two approaches compared. Energy Policy 21, 691-702.
- Wanli, Y. 1985. Daqing oil field, People's Republic of China: A giant field with oil of nonmarine origin. Bulletin of the American Association of Petroleum Geologists 69, 1101-1111.
- Yeh, H., and S. Epstein. 1981. Hydrogen and carbon isotopes of petroleum and related organic matter. Geochimica et Cosmochimica Acta 45, 753-762.

**TABLE 1.** Global CO<sub>2</sub> Emissions from Fossil Fuel Production and Cement Manufacture During 1950-1991. Total is the sum of CO<sub>2</sub> emissions from the production of gas, liquid and solid fuels, gas flaring, and cement manufacture in million metric tonnes C. The 1991 emissions include 123 and 7.3 million metric tonnes C from oil consumed and gas flared during the Kuwaiti oil field fires.

YEAR	TOTAL	GASES	LIQUIDS	SOLIDS	FLARING	CEMENT	$\delta^{13}\text{C}$
1950	1638	97	423	1077	23	18	-25.86
1951	1775	115	479	1137	24	20	-26.00
1952	1803	124	504	1127	26	22	-26.11
1953	1848	131	533	1132	27	24	-26.16
1954	1871	138	557	1123	27	27	-26.21
1955	2050	150	625	1215	31	30	-26.24
1956	2185	161	679	1281	32	32	-26.29
1957	2278	178	714	1317	35	34	-26.37
1958	2338	192	732	1344	35	36	-26.42
1959	2471	214	790	1390	36	40	-26.51
1960	2586	235	850	1419	39	43	-26.61
1961	2602	254	905	1356	42	45	-26.79
1962	2708	277	981	1358	44	49	-26.91
1963	2855	300	1053	1404	47	51	-27.00
1964	3016	328	1138	1442	51	57	-27.12
1965	3154	351	1221	1468	55	59	-27.23
1966	3314	380	1325	1485	60	63	-27.35
1967	3420	410	1424	1455	66	65	-27.55
1968	3596	445	1552	1456	73	70	-27.70
1969	3809	487	1674	1494	80	74	-27.85
1970	4084	516	1838	1564	87	78	-27.89
1971	4235	554	1946	1564	88	84	-28.01
1972	4403	583	2055	1580	94	89	-28.07
1973	4641	608	2240	1588	110	95	-28.13
1974	4649	618	2244	1585	107	96	-28.16
1975	4622	623	2131	1679	93	95	-28.12
1976	4889	647	2313	1717	109	103	-28.16
1977	5028	646	2389	1780	104	108	-28.09
1978	5076	674	2383	1796	107	116	-28.17
1979	5358	714	2534	1892	100	119	-28.19
1980	5292	726	2407	1950	89	120	-28.20
1981	5121	736	2270	1922	72	121	-28.24
1982	5081	731	2176	1985	69	121	-28.21
1983	5072	733	2161	1991	63	125	-28.20
1984	5237	785	2185	2083	57	128	-28.26
1985	5413	818	2170	2239	55	131	-28.23
1986	5601	835	2276	2300	53	137	-28.17
1987	5727	897	2287	2351	48	143	-28.28
1988	5953	940	2394	2413	55	152	-28.29
1989	6068	976	2429	2454	53	156	-28.31
1990	6098	1004	2482	2393	62	157	-28.42
1991	6188	1024	2591	2342	70	162	-28.45

**TABLE 2.** Changing Estimates of Carbon Dioxide Emissions from Fossil Fuel and Cement Production Based on Successive Annual Releases of U.N. Energy Data. There is about an 18 month lag between the end of a year and the first release of the U.N. energy data for that year. References are for publication of the CO<sub>2</sub> emissions estimates based on annual U.N. energy data. All emissions are given in millions of metric tonnes carbon.

Emission Year	Energy Data Release Date				
	1993 <sup>1</sup>	1992 <sup>2</sup>	1991 <sup>3</sup>	1990 <sup>4</sup>	1989 <sup>5</sup>
1991	6188	-----	-----	-----	-----
1990	6098	6097	-----	-----	-----
1989	6068	6024	5967	-----	-----
1988	5953	5912	5897	5893	-----
1987	5727	5698	5661	5680	5650

<sup>1</sup> this work

<sup>2</sup> previously unpublished data

<sup>3</sup> Marland and Boden (1991)

<sup>4</sup> Marland (1990)

<sup>5</sup> Marland and Boden (1989)

**TABLE 3.** Comparison of Selected Annual CO<sub>2</sub> Emissions Estimates Based on 3 Different Time Series of Energy Data. The second column contains CO<sub>2</sub> estimates based on the Etemad et al. (1991) energy data. The third column contains the CO<sub>2</sub> estimates of Keeling (1973), based on energy data largely from the U.N., circa 1973. The fourth column is the CO<sub>2</sub> estimates based on the 1993 U.N. energy data. Note that this table does not include carbon emissions from cement manufacture. All emissions in millions of metric tonnes C.

Year	Etemad et al., 1991	Keeling, 1973	U.N., 1993
1751	0.10		
1761	0.12		
1771	0.15		
1781	0.19		
1791	1.05		
1800	8		
1810	11		
1820	14		
1830	25		
1840	34		
1850	55		
1860	93	93	
1870	151	145	
1880	238	227	
1890	365	350	
1900	548	525	
1910	837	805	
1913	967	929	
1928	1093	1091	
1938	1173	1161	
1950	1635	1613	1620
1951		1744	1755
1952		1767	1781
1953		1809	1824
1955	2045		2020
1960	2623		2543
1965	3234		3095
1970	4194		4006
1975	4720		4527
1980	5408		5172
1985	5449		5282



**TABLE 4.** Preliminary Cumulative Emissions of Carbon to the Atmosphere Based on Fossil Fuel Production. Based on energy data from Etemad et al. (1991) for 1751-1949 and from U.N. (1993) for 1950-1991. Annual emissions in million metric tonnes C and cumulative emissions in billion metric tonnes C. Only selected years used to create Figure 3 are shown here. Note that carbon emissions from cement manufacture are not included.

Year	Annual Emissions	Cumulative Emissions
1751	2.6	0.0026
1760	2.9	0.027
1770	3.6	0.059
1780	4.2	0.10
1790	5.6	0.15
1800	7.8	0.22
1810	11	0.31
1820	14	0.44
1830	25	0.63
1840	34	0.92
1850	55	1.4
1860	93	2.1
1870	151	3.3
1880	238	5.3
1890	365	8.3
1900	548	13
1910	837	20
1913	967	22
1928	1093	38
1938	1173	49
1949	1635	65
1950	1620	66
1960	2543	87
1970	4006	119
1980	5172	166
1990	5941	220
1991	6026	226

**TABLE 5.**  $\delta^{13}\text{C}$  Isotopic Values Used for Carbon Isotope Calculations. Data sources cited in text.

<u>Fuel or Cement</u>	$\delta^{13}\text{C}$ (PDB)
Coal	-24.1
Natural Gas	-44.0
Gas Flaring	-40.0
Cement	0.0
Petroleum (mode)	-26.5
<u>Top petroleum producers</u>	
Canada	-29.9
China	-29.3
Egypt	-28.5
Indonesia	-27.7
Iran	-26.8
Iraq	-27.1
Kuwait	-27.3
Libya	-28.2
Mexico	-26.5
Nigeria	-26.6
Norway	-28.9
Saudi Arabia	-26.4
USSR, Former, 1950-1965	-28.0
1966-1975	-28.1 to -29.0
1976-1979	-29.2 to -29.8
1980-1991	-30.0
United Arab Emirates	-27.0
United Kingdom	-29.6
United States of America	-26.5 to -27.525
Venezuela	-26.1

## FIGURE CAPTIONS

**FIGURE 1.** Global CO<sub>2</sub> Emissions from Fossil Fuel Production and Cement Manufacture During 1950-1991.

**FIGURE 2.** Three CO<sub>2</sub> Emissions Scenarios for Kuwait. Figure 2a includes no emissions resulting from the oil field fires. Figure 2b contains gas flaring emissions from the oil field fires and is the set of curves that would be calculated from the U.N. (1993) data. Figure 2c contains both emissions from gas flaring and oil consumed during the 1991 oil field fires. Individual curves for emissions from natural gas and coal consumption, and cement manufacture are not shown for clarity. However, these emission estimates are included in the total emissions curve. Figures 2a, 2b and 2c are identical except in how emissions in 1991 are allocated.

**FIGURE 3.** Preliminary Cumulative Emissions of Carbon to the Atmosphere Based on Fossil Fuel Production. Based on energy data from Etemad et al. (1991) for 1751-1949 and from U.N. (1993) for 1950-1991. Note that carbon emissions from cement manufacture are not included. The boxes indicate years with calculated annual CO<sub>2</sub> emissions (Table 4). Between boxes, emissions are linearly extrapolated.

**FIGURE 4.** The Latitudinal Change in CO<sub>2</sub> Emissions From 1980 to 1989 as Seen in 5° Bands. There is a small decrease in 1989 emissions from 1980 emissions in the 50-55°N latitude band. Energy consumption data from 1980 and 1989 (Marland and Boden, 1989) was distributed within countries by 1980 relative-consumption data (Marland et al., 1985).

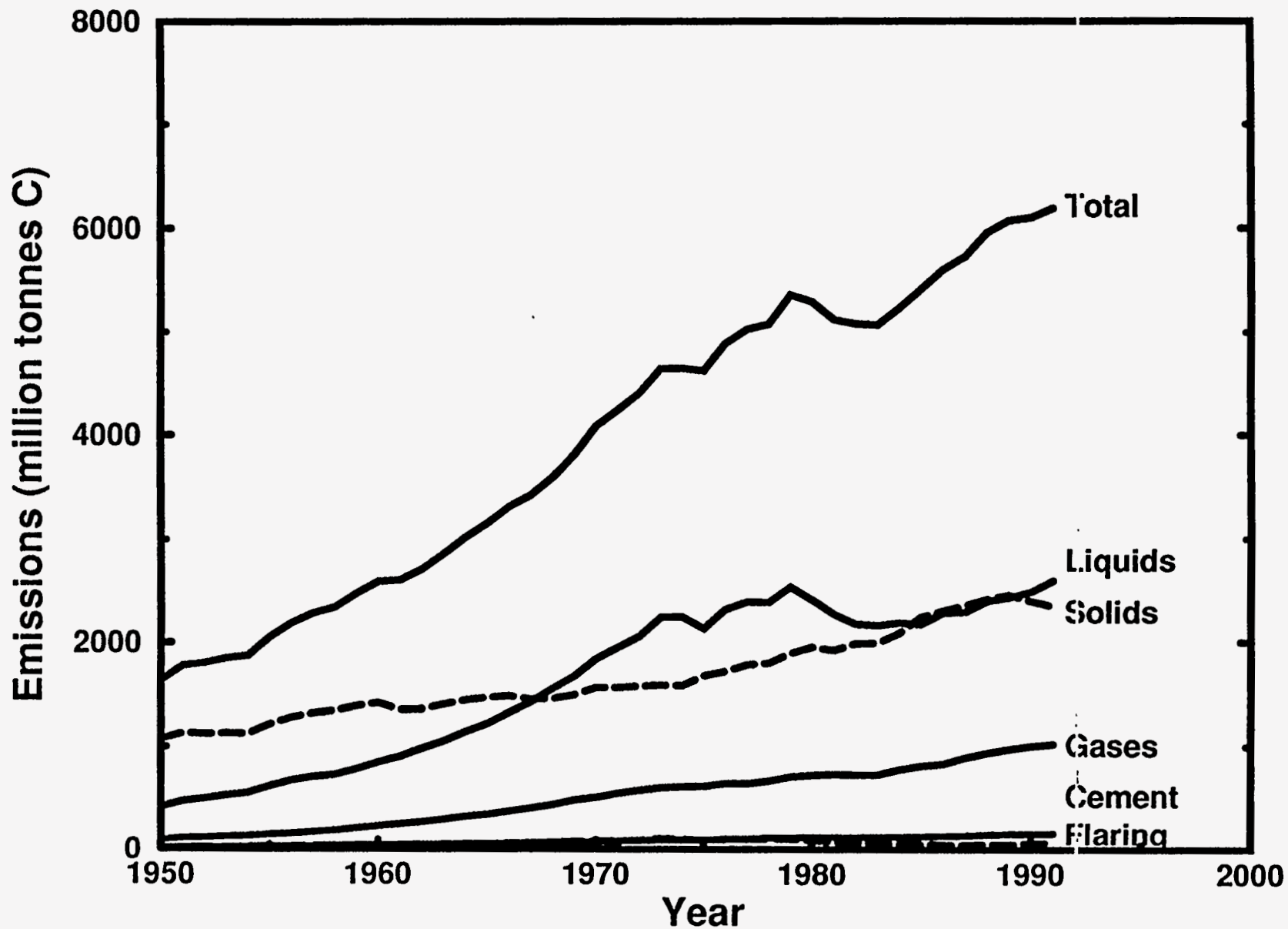
**FIGURE 5.**  $\delta^{13}\text{C}$  of Annual CO<sub>2</sub> Emissions from Fossil Fuel Production and Cement Manufacture. The upper curve was calculated with the  $\delta^{13}\text{C}$  values suggested by Tans (1981) and the lower curve was calculated with the  $\delta^{13}\text{C}$  values described herein. For years before 1950, the lower curve was calculated with a  $\delta^{13}\text{C} = -26.52$  for oil which was the 1950 production-weighted value. Both curves utilize the same fuel production data (Keeling, 1973 for pre-1950 and U.N., 1993 for post-1949). Cement manufacturing data (Solomon, 1993) are included for post-1949 years only and their inclusion cause the slight increase seen in both curves for 1950.

DISPLAYED EQUATIONS

$$\text{CO}_{2,i} = \text{FP}_i \times \text{FO}_i \times \text{C}_i \quad (1)$$

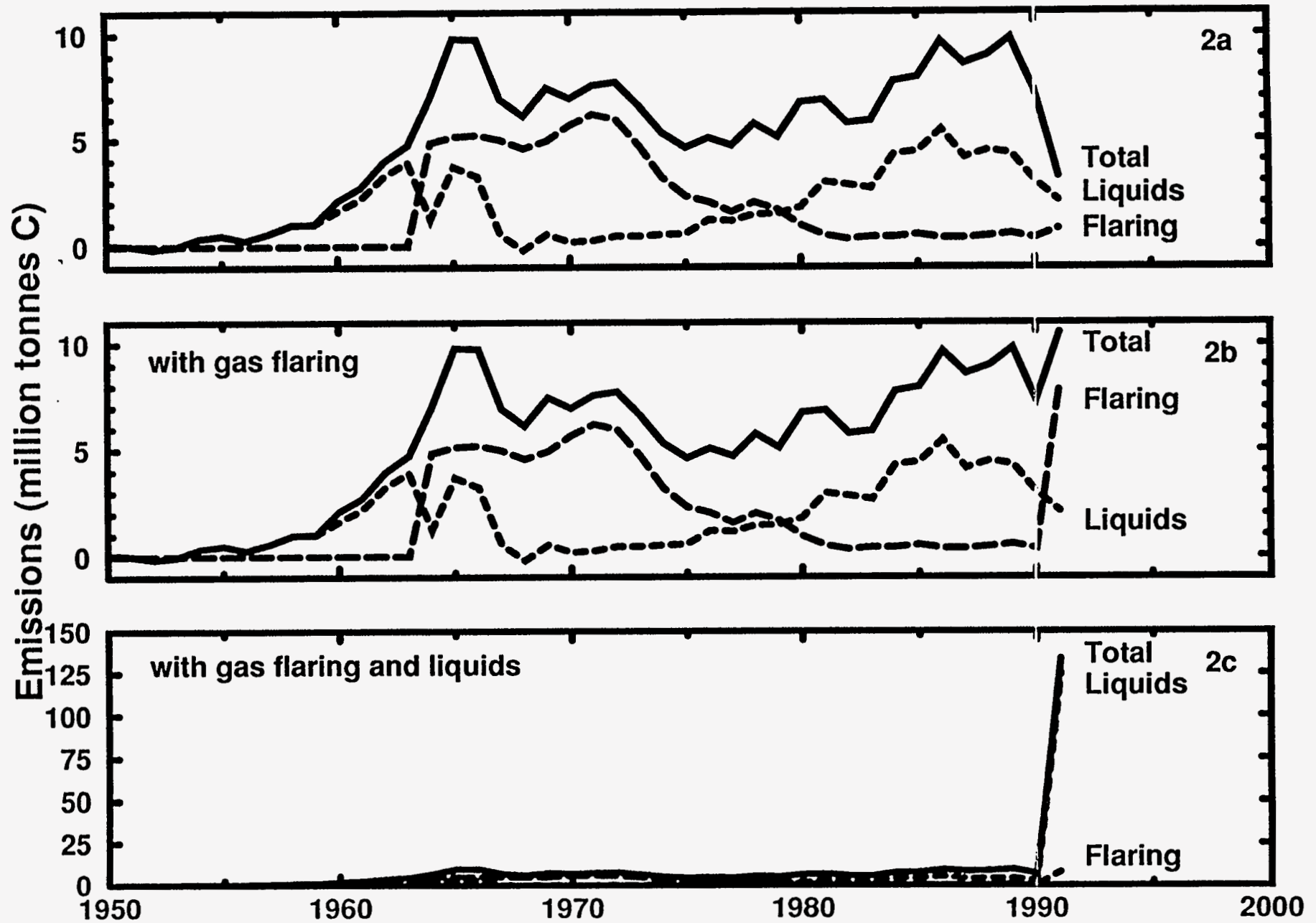
# Global Carbon Dioxide Emissions

from Fossil Fuel Production and Cement Manufacture Data



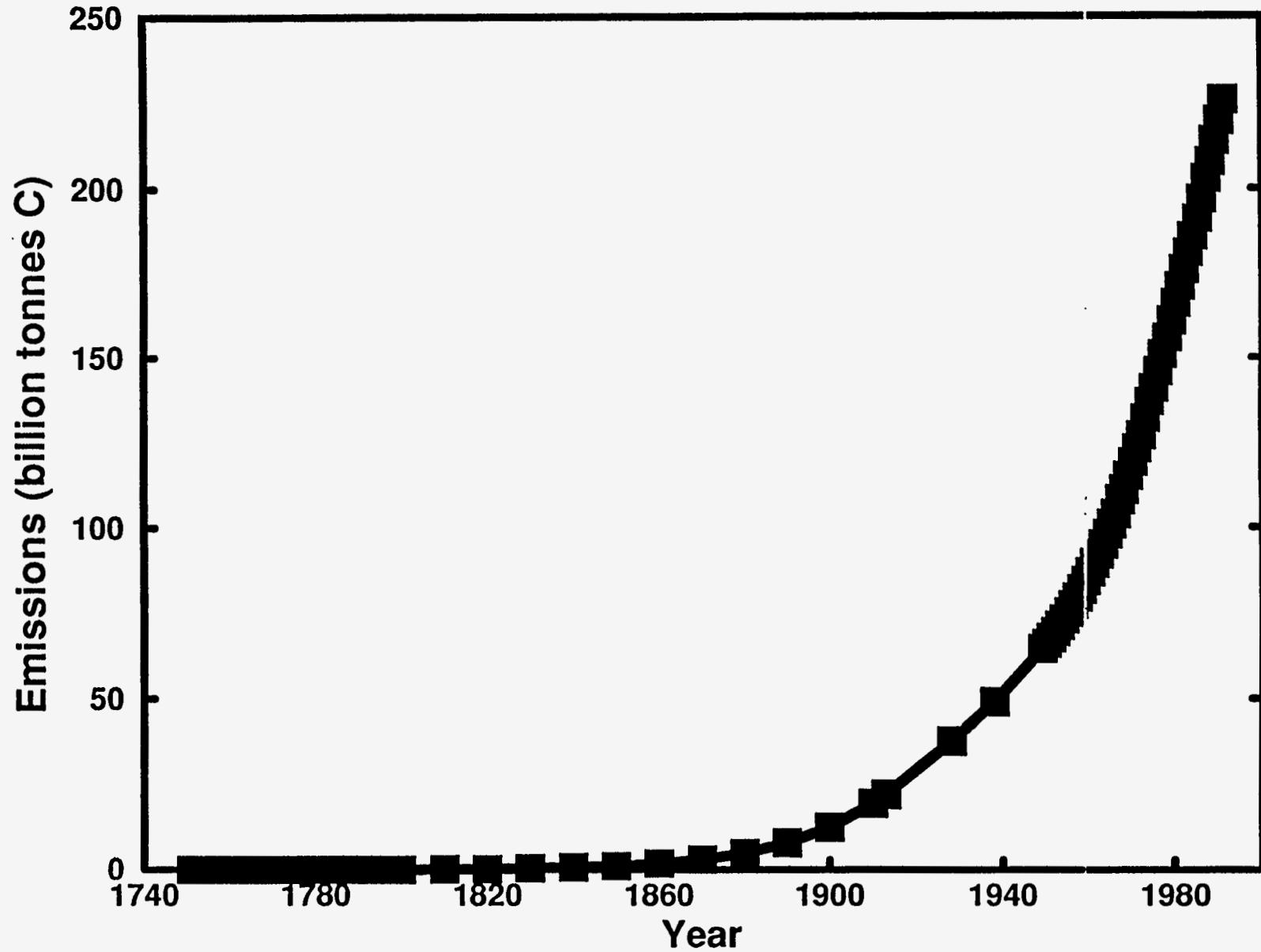
# Kuwaiti Carbon Dioxide Emissions

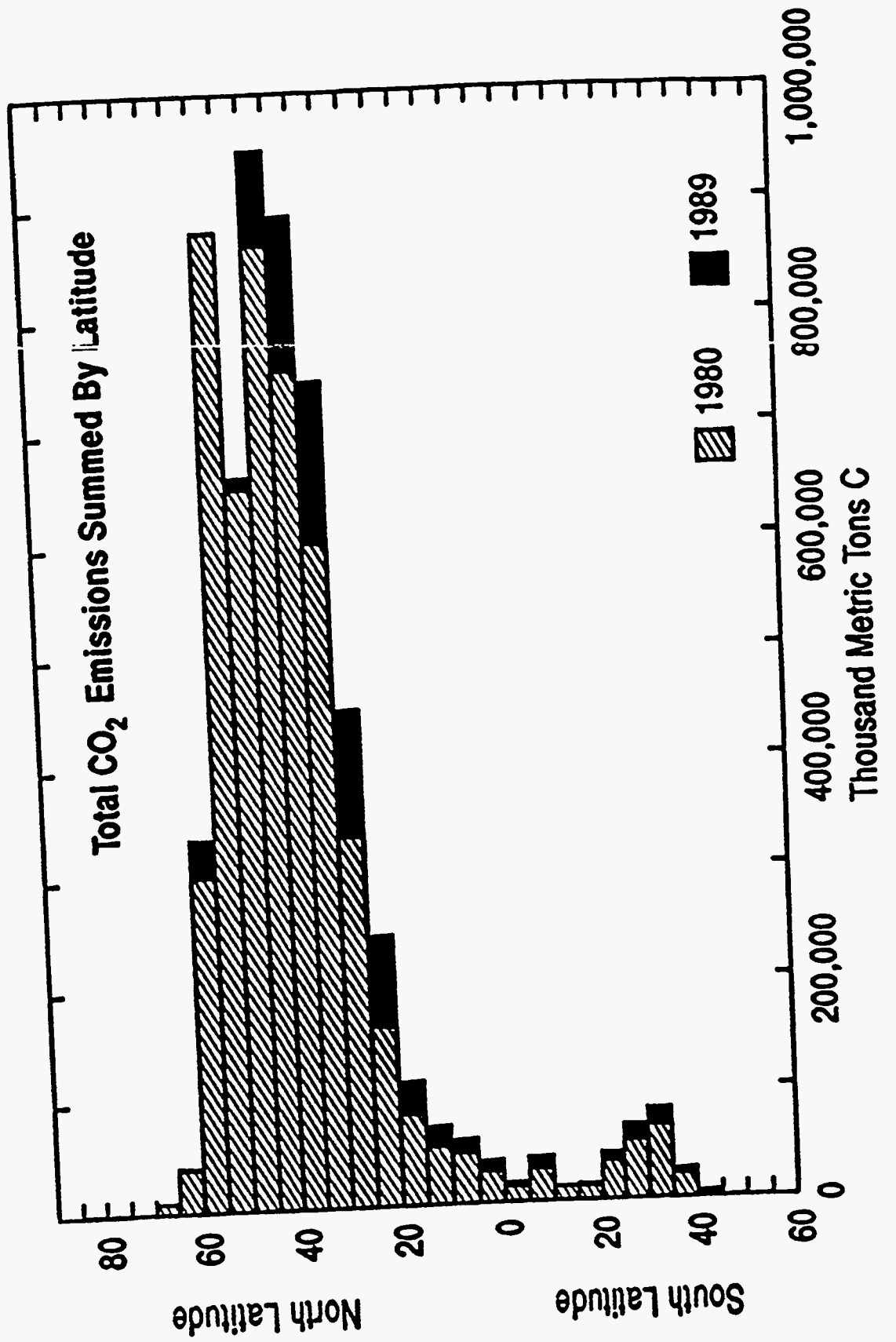
Gases, Solids and Cement Not Shown



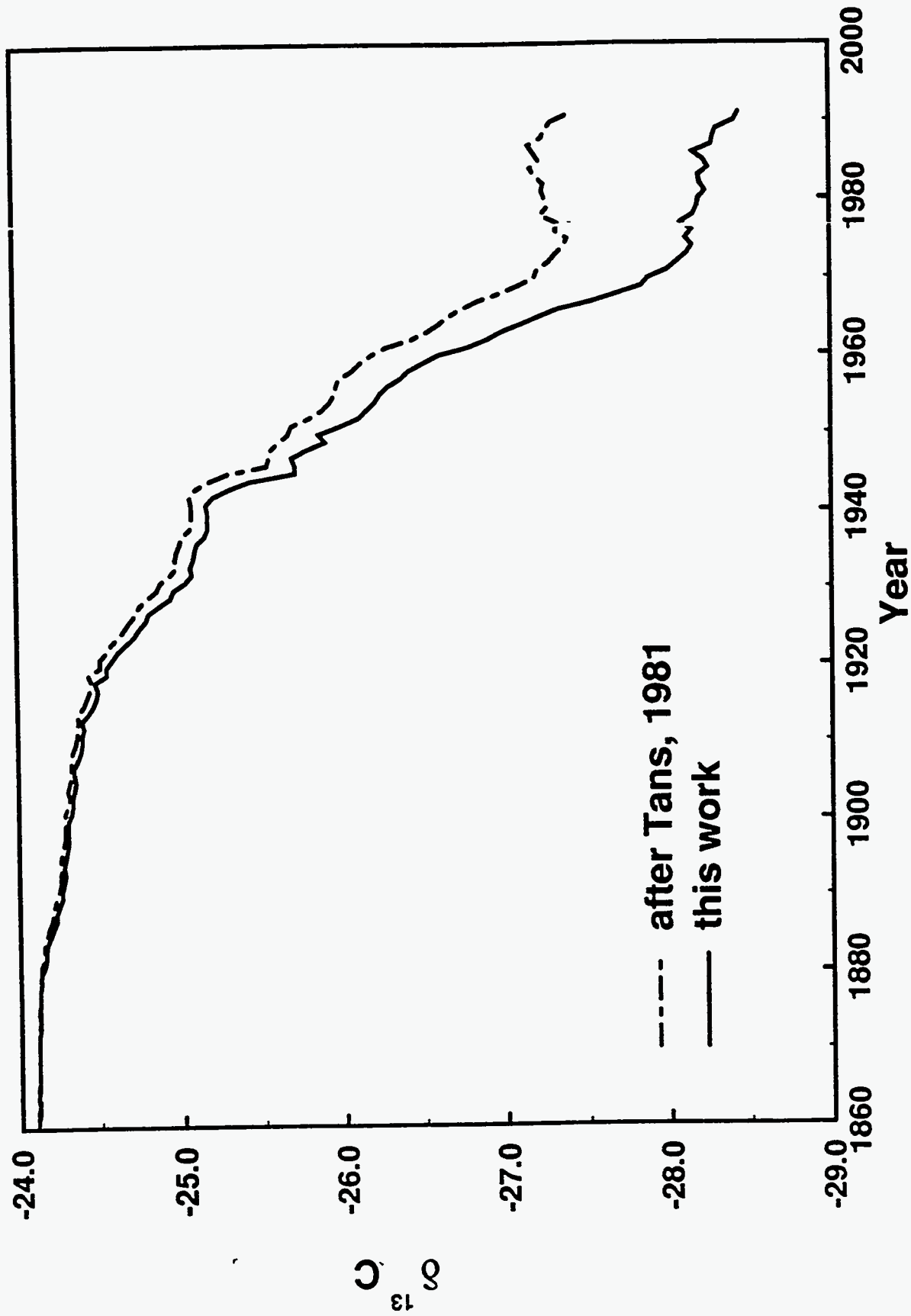
# Cumulative Emissions from Fossil Fuels

Based on Etemad et al. (1991) and U.N. (1993) Data









DISPLAYED EQUATIONS

$$\text{CO}_{2j} = \text{FP}_i \times \text{FO}_i \times \text{C}_i \quad (1)$$