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Assessing Historical Global Sulfur Emission Patterns For the Period ~~1850-1970~~ **BEST**

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EXECUTIVE SUMMARY

S.1 Introduction

Anthropogenic sulfur dioxide emissions from energy-producing and metal production activities have become an important factor in better understanding the relationship between humans and the environment. Concerns about (1) acid rain effects on the environment and (2) anthropogenic aerosols affecting possible global change have prompted interest in the transformation and fate of sulfur in the environment.

One step in assessing the importance of sulfur emissions is the development of a reliable regional emission inventory of sulfur as a function of time. In the past, there have been several attempts to identify historical trends of sulfur dioxide emissions. In most cases, the data sets were obtained from various sources with different spatial resolution. Several others have estimated global S/SO₂ emissions for shorter time periods. Large discrepancies among the approximations reflect the many uncertainties associated with estimating S/SO₂ emissions.

Beginning in September 1994, under a grant from the U.S. Department of Energy, A.S.L. & Associates, its subcontractor, Center for Air Pollution Impact and Trend Analysis (CAPITA), and consultant Dr. Peter Brimblecombe developed a database that allows for annual estimates of the global emissions of sulfur from 1850 to 1990. A special effort was made to ensure that a common methodology was applied across all years and countries for the estimation of the sulfur emissions. The use of a consistent methodology makes it possible to produce global totals by adding estimates from each country. In addition, the use of a consistent approach makes it possible to easily modify the database and immediately observe the magnitude of the changes on

national, regional, or global estimates. The emission estimates for each country are based on the net production (i.e., production plus imports minus exports), percent sulfur, and sulfur retention information associated with that country's activities. Fine temporal resolution information is available from the database; thus, changes associated with specific historical events (e.g., wars, depressions, etc.) are clearly observed in the emission inventory on a regional, national, or global basis. Uses for the completed global sulfur emission inventory include (1) input into global pollution models; (2) comparing the global sulfur emission patterns with atmospheric sulfur flux data; and (3) forming the basis for global sulfur emission projections.

The objective of this research effort was to create a homogeneous database for historical sulfur emission estimates for the world. The time from 1850-1990 was selected to include the period of industrialization from the time the main production of fuels and minerals began until the most recent year for which complete production data exist. This research effort attempts to correct some of the deficiencies associated with previous global sulfur emission estimates by (1) identifying those production activities that resulted in sulfur emissions by country and (2) calculating historical emission trends by country across years. However, we recognize that there are many uncertainties associated with estimating emissions because of incomplete data on production, transfer, and consumption rates; most particularly the poorly quantified emission factors and retention rates.

An important component of this study was the comparison of our sulfur emission results with those of previous studies. Data were available from other sources using different methodologies, such as United States emission estimates from the U.S. Environmental Protection Agency. Such data were used

only for purposes of comparison with the estimated results derived from this research effort. One global inventory of sulfur emissions from anthropogenic sources used for comparative purposes was compiled for 1985 by an international group under the umbrella of the Global Emissions Inventory Activity of the International Global Atmospheric Chemistry Programme. Appendix A of this report summarizes the analysis protocol applied and the results associated with the study to estimate global sulfur emissions for 1985 and 1990. Many of published regional and global sulfur emission estimates mentioned in the report were used to compare with the ASL/CAPITA estimates.

An important aspect of creating an emission inventory is the identification of levels associated with natural emissions. Although the main report of this research effort focused on the estimation of anthropogenic historical emissions of sulfur, two groups of authors were asked to address natural emissions so as to qualitatively place the anthropogenic emissions into perspective with total global sulfur emissions (i.e., anthropogenic and natural). Although there is some uncertainty associated with estimating historical global emissions from anthropogenic sources, the uncertainties associated with natural emissions are much greater. Appendices B and C discuss natural emissions associated with sea salt, marine, volcanic activity, wind-blown soil (aeolian activity), and biomass burning. The natural sulfur emission information in Appendices B and C is provided for background to the interested reader.

The estimate of global sulfur emissions over time was reconstructed using a production-driven material approach. The net production is equated with consumption. The material balance approach assumes that atmospheric sulfur emissions are the consequence of sulfur removal from long-term

geochemical reservoirs (e.g., fossil fuels and ore deposits) and transferring the sulfur to other geochemical reservoirs, such as oceans and surface soil. During the transit between the long-term geochemical reservoirs, a fraction of the human-induced sulfur flow passes through the atmosphere. The focus of this work is on the estimation of the sulfur flow through the atmosphere (i.e., the atmospheric sulfur emission rates). In particular, the objective is to develop a picture of atmospheric sulfur emissions by country, as the emissions fluctuate over time from 1850 to 1990 due to production, export, and import material flows. The sulfur emission rate to the atmosphere is computed by multiplying the net production rate of fuels and metals with their sulfur content and by a factor incorporating sulfur retention. The resulting product yields the estimated sulfur emission for a given country, year, and fuel/metal type. Specific attention has been given in this report to flue gas desulfurization (FGD) controls used globally on coal-burning facilities, as well as low-sulfur coal switching strategies implemented in the United States, beginning in 1973.

S.2 Production

The developed production database is a homogeneous trend data set of 16 variables, (i.e., production, import, and export variables for hard coal, brown coal, crude petroleum, and natural gas, as well as production data only for the metals, copper, zinc, lead, and nickel). Some of the interesting conclusions reached using the production component of the database include:

1. The production of anthracite and bituminous hard coal exceeds brown coal production by approximately a factor of 3.
2. The first growth of global coal production occurred between 1880 and 1910, followed by a plateau until about 1950. A second major

rise is observed between 1950 and 1990. The production of world coal has doubled since 1950.

3. Brown coal has become an increasing fraction of the total coal production. By 1990, hard coal and brown coal production was about 4.75 billion metric tons per year.
4. In 1900, the largest coal producing country was Great Britain, followed by the United States and Germany. In 1930, the United States coal production exceeded Great Britain by a substantial margin. By 1960, the three major coal producing countries were China, the United States, and the former U.S.S.R. This trend continued through 1990, when China became the largest coal producing country, followed by the United States and the former U.S.S.R.
5. The world oil production shows an exponential growth from its onset about 1900 to the early 1970s. However, for the past twenty years, the global production has fluctuated about 10%. The oil import and export indicate that prior to World War II, the international oil trade was insignificant. However, by the 1960s, the international flow of oil (i.e., export) had become about 50% of the global production.
6. The major oil producing countries in 1990 were the former U.S.S.R. (565,500,000 metric tons), the United States (369,679,000 metric tons), and Saudi Arabia (320,375,000 metric tons). Prior to World War II, the United States was the dominant oil producing nation.
7. Using net production (approximating oil consumption), since the turn of the century, the United States has been the largest oil consumer. The abrupt reduction of oil consumption in the 1970s was followed by an increase in the middle 1980s and a slight decrease in the late 1980s. The next major consumer, the former U.S.S.R., showed a sharp rise between 1950 and 1980, but modest change over the past decade. Japan shows little oil consumption prior to 1950, but an exponential growth up to 1970, followed by a slow decay period. For 1990, the major oil consumers are the United States, the former U.S.S.R., China, and Japan, as well as the western European countries.
8. The world production of sulfur containing metals (copper, zinc, lead, and nickel) exhibits a rather varied behavior since 1850. Copper, zinc, and lead have roughly comparable production rates from 1850 to about 1950. From 1950 on, the copper and zinc production have been increasing by a factor of 3-4, while the lead production has only doubled between 1950-1990. Between 1970 and 1990, the global lead production declined. Nickel production has steadily increased from 1930 to 1990 but at much lower magnitude than the other three metals.

9. In 1990, the former U.S.S.R. and Canada were the major nickel producers. The spatial pattern of world copper production for 1990 shows Chile, the United States, and Canada as the most prolific producers. A substantial copper production is also noted in Asia and Africa. During the first half of the century, copper production in the United States prevailed. However, since the 1980s, Chile has become a leading copper producer. Canada, the former U.S.S.R., and Australia are the dominant producers of zinc, along with China, the United States, and Peru. The leading zinc producers had moderate production prior to World War II. In 1990, the major producers of zinc were Canada, Australia, the former U.S.S.R., China, Peru, and the United States. The major lead producing nations in 1990 were Australia, the United States, and the former U.S.S.R. China, Canada, Peru, and Mexico were also significant lead producers. Prior to World War II, the United States lead production was the largest among the nations. However, since 1950, both Australia and the former U.S.S.R. have become the major lead producers.

S.3 Emissions

Focusing on the sulfur emissions database, on a global basis for extended periods, the study's sulfur emission estimates agreed closely with several sets of data which described previous estimates. The current protocol used in this study for deriving sulfur emission estimates generally compares favorably with previously-applied methods. For example, although using a different protocol, the values reported for 1985 by Benkovitz *et al.* (1996) were almost identical to the values estimated in this study (i.e., approximately 65 million metric tons). Similarly, for 1990, the estimates by ASL/CAPITA and those by Benkovitz *et al.* (1996) were approximately 71.5 million metric tons. In general, except for a few countries (e.g., West Germany and Italy), the European estimates from this study compared favorably with those of Mylona (1993), CORINAIR (U.S. EPA, 1995b), and Benkovitz *et al.* (1996). However, some discrepancies were found. For example, the Kato (1996) estimates for Japan were in the range of 37-66% of the sulfur emission estimates made by this study. In addition, the U.S. EPA (1995b) estimates

identified a downward trend of sulfur emissions in the United States from the mid-70s to 1990. On the other hand, this study shows a leveling off of sulfur emissions from the mid-70's to early 80's, a downward trend until the mid-80's, and then a gradual increase into the 1990s. Upon closer investigation, we believe that some of the discrepancy between the ASL/CAPITA sulfur emission estimates and those of the U.S. EPA's may be associated with differences in estimates for the residual fuel consumption. In addition, the U.S. EPA assumes that sulfur dioxide and PM-10 controls are 100 percent effective. For 1990, this study used 85% as the average efficiency of sulfur removal for FGD controls, based on the data received from the International Energy Agency.

This study investigated the possible contribution of several reduction sulfur emission options. It appears that using FGD controls showed only a marginal decrease in sulfur emissions in the United States. On the other hand, in the United States, the use of low-sulfur coals in combustion appears to have had a greater effect on sulfur emission reductions in the United States than the FGD controls. From 1973 through 1990, the average percent of sulfur in coal used for combustion purposes in the United States has decreased substantially and its effect on emissions was clearly observed. On a global scale, similar observations are found when evaluating global sulfur emissions. However, it must be noted that for a specific country, FGD controls have a major impact on its nation's sulfur emissions.

The spatial pattern of global sulfur emissions shows that the United States, the former U.S.S.R., and China were the main sulfur emitters (i.e., approximately 50% of the total emissions) in the world in 1990. For 1990, the top three sulfur-emitting countries account for 53% of the global sulfur emissions. Combustion of anthracite and bituminous hard and brown coal is the

dominant source of anthropogenic sulfur emissions. The sulfur emission trends associated with the combustion of hard coal are mainly due to the United States, China, and the former U.S.S.R. However, historical trends of sulfur emissions for the above three countries are remarkably different. While the United States shows substantial emissions prior to 1940, China and the former U.S.S.R. show virtually no emissions in the first half of the century; however, these two countries contributed greatly to the sulfur emissions in the latter half of this century. Although sulfur emissions appear to have stabilized over the past 20 years in the former U.S.S.R. and the United States, the recent increase in global sulfur emissions appears to be linked to the rapid increases associated with sulfur emissions in mainland China.

Combustion of anthracite and bituminous hard and brown coal is the dominant source of anthropogenic sulfur emissions. The contribution of oil products rose rapidly between 1950 and 1980. However, these rapid increases have not continued. Similarly, sulfur emissions associated with copper smelting peaked in 1974. Therefore, the steady increase of global sulfur emissions since the 1970s is attributable to increases in coal combustion.

The major sulfur emitters from oil consumption are the United States, the former U.S.S.R., and Saudi Arabia, with notable emissions from Mexico, China, and Japan. The historical trends of oil sulfur emissions for the major emitters, the United States, U.S.S.R., and Saudi Arabia, show the early dominance of the United States and the subsequent emergence of the other two countries since the 1950s.

The sulfur emissions from copper show an identical pattern to the copper production, since both sulfur content of ores and the atmospheric emission fraction were assumed to be geographically constant. Since 1910, the sulfur

emission trends for the United States show highly fluctuating values. On the other hand, since 1920, Chile shows a steady increase of copper-related emissions. In 1990, the major sulfur emitters from copper production were Chile, the United States, Canada, the former U.S.S.R., Zambia, Zaire, and Poland. Canada, Australia, the former U.S.S.R. and China produce the major zinc-related sulfur emissions. The lead-related sulfur emission rate in 1990 was highest in Australia, the United States, the former U.S.S.R, China, and Canada. The sulfur emissions associated with nickel production is dominated by the former U.S.S.R. and Canada.

S.4 Accessing the Database

In conclusion, this study has created and used a database that describes production information, percentage of sulfur in fuels and metals, retention factors based on technological removal of sulfur, and sulfur emissions for the period 1850 to 1990. The special effort devoted to ensuring the application of a common methodology across all years and countries for the estimation of emissions makes it possible to (1) produce global totals by adding estimates from each country and (2) easily improve the information contained within the database. To foster international cooperation in the maintenance and improvement of the information contained in the database, following the publication of a peer-review paper, A.S.L. & Associates, in cooperation with its subcontractor and consultant, will provide electronic access to the information through a series of web pages on the internet. Further information can be found by accessing the following internet address:

http://ourworld.compuserve.com/homepages/ASL_ASSOCIATES/

The participants in this research project, by making the data available electronically, encourage joint collaboration in helping to improve the accuracy of the information contained with the database.

1. INTRODUCTION

Anthropogenic sulfur dioxide emissions from energy-producing and metal production activities have become an important factor in better understanding the relationship between humans and the environment (Rodhe, 1989; Legge and Krupa, 1990). Concerns about (1) acid rain effects on the environment and (2) anthropogenic aerosols affecting possible global change (Charlson et al., 1992) have prompted interest in the transformation and fate of sulfur in the environment.

During the last few decades, the potential importance of anthropogenically produced sulfate aerosols to the climate system has been discussed (Charlson et al., 1992). Aerosols theoretically have the ability to cool the atmosphere and are sometimes referred to as 'anti-greenhouse gas.' Estimates of both their magnitude and importance vary regionally from a relatively small influence to one which, in the Northern Hemisphere, can counter the entire greenhouse forcing (Charlson et al., 1992). The Intergovernmental Panel on Climate Change (IPCC) report (IPCC, 1994), has reconfirmed the ability of aerosols to affect the climate system by changing the radiative balance of the atmosphere.

One of the first steps in assessing the importance of sulfur emissions is the development of a reliable regional emission inventory of sulfur as a function of time. There have been several attempts to identify trends of sulfur dioxide emissions since the middle 1800s (Bettelheim and Littler, 1979; Dignon and Hameed, 1989; Husar and Husar, 1990; Mylona, 1993; Örn and Rodhe, 1995). Mylona (1993) quantified trends in Europe from 1880 to the present period. Iversen (1993) presented a subset of the data described by Mylona (1993). Örn and Rodhe (1995) estimated sulfur emissions for every 10th year

from 1860 to 1985. The data sets were obtained from various sources with different spatial resolution. However, although the data were available on diskette, the results from the study have not been published in the open literature. Accordingly, at the request of the authors, we have not compared our results with the unpublished data by Örn and Rodhe. Several others have estimated global S/SO₂ emissions for shorter time periods (e.g., Kellogg et al., 1972; Dignon, 1992; Varhelyi, 1985; Cullis and Hirschler, 1980; Möller, 1984; Spiro et al., 1992). Large discrepancies among the approximations reflect the many uncertainties associated with estimating S/SO₂ emissions. Besides global determinations, continental or national estimates of S/SO₂ emissions have been made (e.g., Gschwandtner et al., 1986; Placet et al., 1990; Fujita et al., 1991; Kato and Akimoto, 1992).

Beginning in September 1994, under a grant from the U.S. Department of Energy, A.S.L. & Associates, its subcontractor, Center for Air Pollution Impact and Trend Analysis (CAPITA), and consultant Dr. Peter Brimblecombe developed a database that allows for annual estimates of the global emissions of sulfur from 1850 to 1990. Special effort was devoted to ensuring that a common methodology was applied across all years and countries for the estimation of emissions. The use of a consistent methodology makes it possible to produce global totals by adding estimates from each country. In all cases, the emission estimates for each country are based on the net production (i.e., production plus imports minus exports), percent sulfur, and sulfur retention information associated with that country's activities (Husar, 1986). If data were available from other sources using different methodology, such as United States emission estimates from the U.S. Environmental Protection Agency, such data were used only for purposes of comparison with

the estimated results derived from this research effort. Fine temporal resolution information is available from the database; thus, changes associated with specific historical events (e.g., wars, depressions, etc.) are clearly observed in the emission inventory on a regional, national, or global basis. Uses for the completed global sulfur emission inventory include (1) input into global pollution models; (2) comparing the global sulfur emission patterns with atmospheric sulfur concentration data; and (3) forming the basis for global sulfur emission projections.

This research effort attempts to correct some of the deficiencies associated with previous global sulfur emission estimates by (1) identifying those production activities that resulted in sulfur emissions by country and (2) calculating historical emission trends by country across years. However, we recognize that there are many uncertainties associated with estimating emissions because of incomplete data on production, transfer, and consumption rates, as well as poorly quantified emission factors.

An important component of this study was the comparison of our sulfur emission results with those of previous studies. One global inventory of sulfur emissions from anthropogenic sources used for comparative purposes was compiled for 1985 by an international group under the umbrella of the Global Emissions Inventory Activity (Benkovitz and Graedel, 1992) of the International Global Atmospheric Chemistry Programme. The regional inventories used include the NAPAP regional inventories for the United States and Canada to 60°N (Saeger *et al.*, 1989); EMEP and CORINAIR85 for Europe (Bouscaren, 1992; Sandnes and Styve, 1992); Kato and Akimoto (1992), and Tonooka (personal communication, 1993) for Asia; Carnovale (Horseman and Carnovale, 1989; Carnovale *et al.*, 1992) for Australia; and Loyd (personal

communication, 1993) for South Africa. SO_x emissions for other regions of the globe were taken from a "default" inventory which was based on the work by Spiro et al. (1992) updated to 1985. The work and results are described in an article by Benkovitz et al. (1996). A global inventory of anthropogenic sulfur emissions for 1990 was developed as a collaborative effort among RIVM, Bilthoven (The Netherlands), IMW-TNO, Delft (The Netherlands), and Brookhaven National Laboratory, Upton (NY, USA). The Dutch effort is part of the Emission Database for Global Atmospheric Research (EDGAR) project (Baars et al., 1991; Berdowski, 1992; Olivier et al., 1994). Appendix A summarizes the analysis protocol applied by Benkovitz et al. (1996) and the results associated with their study to estimate global sulfur emissions for 1985 and 1990. The Appendix serves as a stand alone document.

An important aspect of creating an emission inventory is the identification of levels associated with natural emissions. Although the main report of this research effort focused on the estimation of anthropogenic historical emissions of sulfur, two groups of authors were asked to address natural emissions so as to place the anthropogenic emissions into perspective with total global sulfur emissions (i.e., anthropogenic and natural). It is recognized that although there is some uncertainty associated with estimating historical global emissions from anthropogenic sources, the uncertainties associated with natural emissions is much greater. Therefore, the natural sulfur emission information in Appendices B and C is provided as a first level estimate. The two appendices are provided for background information for the interested reader. In some cases, the two appendices present conflicting information. However, because of the large uncertainties associated with estimating natural sulfur emissions, no attempt has been made to resolve the

conflicting areas. Appendices B and C discuss natural emissions associated with sea salt, marine, volcanic activity, wind-blown soil (aeolian activity), and biomass burning. Sulfur emission rates of volcanoes have recently begun to be estimated based on surface measurements. Lacking direct measurements, various methodologies to estimate sulfur emissions have been developed and applied to obtain estimates of the contribution of volcanoes to the global atmospheric sulfur budget. Appendix C lists compiled estimates of sulfur emissions from volcanic activity for the years 1985 and 1990. For those wishing to obtain the electronic version of the database, a series of web pages is being created for this purpose. Further instructions can be obtained by accessing the following internet address:

http://ourworld.compuserve.com/homepages/ASL_ASSOCIATES/

2. APPROACH

The objective of this research effort was to create a homogeneous database for historical sulfur emission estimates for the world. The time domain of 1850-1990 was selected to include the period of industrialization from the time the main production of fuels and minerals began until the most recent year for which complete production data exist.

The estimate of global sulfur emissions over time was reconstructed using a *production-driven material approach* (Husar, 1986). Simpler versions of the methodology have been used by several investigators (Cullis and Hirschler, 1980, Spiro et al., 1992).

The material balance approach assumes that atmospheric sulfur emissions are the consequence of sulfur removal from long-term geochemical reservoirs (e.g., fossil fuels and ore deposits) and transferring the sulfur to other

geochemical reservoirs, such as oceans and surface soil. During the transit between the long-term geochemical reservoirs, a fraction of the human-induced sulfur flow passes through the atmosphere. The focus of this work is on the estimation of the sulfur flow through the atmosphere (i.e., the atmospheric sulfur emission rates). In particular, the objective is to develop a picture of atmospheric sulfur emissions by country, as the emissions fluctuate over time since 1850 due to production, export, and import material flows.

The methodology of production-driven sulfur emission estimation relies on the estimation of the extraction rate of sulfur bearing fuels and metals (i.e., the production rate of fuels and metal ores). The production information originates from national statistical tables that account for various mining and processing activities in individual countries. Once the production-driven sulfur emission estimates are made, the next step is to estimate the sulfur content of fuels and minerals. The sulfur content is estimated by using information derived from the chemical analysis of the mobilized fuels and minerals. The chemical information is derived from an analysis for a specified time, rather than continuously monitored. Such analyses are generally adequate, since the individual fuel and ore reservoirs have reasonably well defined and stable sulfur content.

Fuel combustion and thermal metal smelting liberate a fraction of the solid sulfur into gaseous sulfur dioxide, which is emitted to the atmosphere. A fraction of the mobilized sulfur is retained in the fuel and mineral residues, such as flyash. Another fraction is recovered from the gaseous form as a useful sulfur byproduct or scrubbed from the gases as solid waste. Solid sulfur retention due to the above processes can be estimated from process analysis at the combustion site.

For fossil fuels there is a significant international export-import trade that physically separates the locations of production and consumption. For this reason, the sulfur emission computations utilize a net sulfur production. The net production includes the sulfur production within the country, plus the imports, minus the exports. Assuming no accumulation of fuels, the net production equals the consumption of fuels in a given country.

The sulfur emission rate to the atmosphere is computed by multiplying the net production rate of fuels and metals with their sulfur content and by a factor incorporating sulfur retention. The resulting product yields the estimated sulfur emission for a given country, year, and fuel/metal type. Specific attention has been given to flue gas desulfurization (FGD) controls used globally on coal-burning facilities, as well as low-sulfur coal switching strategies implemented in the United States, beginning in 1973. Figure 1 illustrates the average percent sulfur content of coal received at electric utilities in the United States for the period 1973-1990 (Energy Information Administration, 1981, 1986, 1991).

FGD controls have been implemented beginning around 1972. Using the cumulative total of thermal generating capacity information by year supplied by the International Energy Agency (IEA) in Paris (personal communication) and the cumulative total of FGD capacity (IEA London, personal communication), it was possible to determine the percentage of the FGD installed capacity by country by year (Table 1). Based on information received from the IEA London (personal communication), the average efficiency of FGD controls by year was calculated (Table 2). Using information obtained from OECD (1973-1991), the fraction of coal used in power plants was obtained by country and year; this

information was then combined with the above data and used in the final emission calculations.

The sulfur emission database consists of three data sets: the production (which includes import and export data) of sulfur containing fuels and metals, the sulfur content of these materials, and the sulfur release factor to the atmosphere. In general, all three factors are three-dimensional variables, depending on country, year, and fuel/metal type (i.e., coal, oil, zinc, lead, copper, and nickel). In our analysis, the fuels/metal production was taken to be three dimensional. With the exception of the United States, the sulfur content was assumed to depend on the country and fuel/metal, but not on time. On the other hand, the sulfur release factor to the atmosphere was assumed to depend on year and fuel/metal but not on the country. Because the available data were incomplete, a more detailed breakdown was not possible at this time.

The main database that drives the creation of the emission inventory is the production of fuels and minerals. The three dimensions of the production database are time, country, and fuels/metals. The three-dimensional data structure was created by using the best available data and approximation algorithms. The problems in accomplishing this task were that the available data were fragmented, sometimes inconsistent, and incomplete. The approach required accessing data from multiple sources, reconciling the differences in units and nomenclature, and filling in missing data by suitable estimates.

The main source of historical data for fuels and minerals were the excellent data compilations by Mitchell (1981, 1982, 1983). The Mitchell data collection covered the period from approximately 1850 through 1975 and included many variables in addition to the fuels and metals reported in the study. The earliest available data varied depending on the country and the

production parameter. Where data were unavailable, we linearly extrapolated backwards from the first available data point to the beginning of major production. For coal and metals, the beginning of the production was assumed to be 1850 and for oil, 1900. Where data gaps existed (e.g., war times), linear interpolation between the available time periods was used.

The Mitchell data set reports the production for individual countries as the nations existed in a given epoch. Due to the emergence and disappearance of individual countries, the production data for some countries may exhibit sharp rises and drops during political and geographical rearrangement of countries. When countries were not in existence, data were forced to zero. For many African countries that have changed names, the most recent names were used. In order to cope with the dynamic transitions in our database, we retained the cumulative list of all the countries for which fuels and metals production were reported. Double accounting of production was avoided by setting the production to zero for any country outside the time range of its existence. The result is a list of 234 countries that have data during the 1850-1990 period.

The relevant variables listed in the Mitchell data set include anthracite coal, bituminous hard coal, bituminous brown coal, crude petroleum, and natural gas, as well as the metal content of mined copper, zinc, lead, and nickel. We are aware that in some cases anthracite is referred to as hard coal, bituminous as soft coal, and lignite as brown coal. However, in our analysis, we made the decision to combine anthracite coal with bituminous hard coal and label them "hard coal." This was because the bituminous brown coal identified in the Mitchell data set was labeled "brown coal." The low grade lignite form of coal was included by Mitchell under another brown coal

category. For fuels, the production data were augmented by the available import and export figures for each country. For metals, only production data were used due to our interest in the emissions associated with their production.

To supplement the Mitchell production data set, a second major material production dataset (Marland and Boden, 1994), prepared by the Carbon Dioxide Information Analysis Center (CDIAC), was used. The CDIAC data set was originally compiled for estimating global carbon dioxide emission trends. However, the data were useful for our research effort. The CDIAC database covered the period 1950-1990 and included fuel production and export import data, but not data for metals production. The CDIAC fuel production data were acquired from the United Nations Energy database. Marland and Rotty (1994) estimate that the uncertainty of the global fuel energy data is about 10%. However, the estimation of uncertainty for the fuel production of individual countries can be greater. The CDIAC production data set divided coal into two categories: Coal Production and Lignite-Brown Coal. For our analysis, Coal Production was identified as "hard coal" and Lignite-Brown Coal was identified as "brown coal." The Mitchell coal data were compared with the CDIAC fuel production database for overlapping years (see below) using the hard and brown coal categories as identified in this study and agreement was observed. All of the countries matched in the reporting, except a few where total coal matched, but the categories did not. For China, Iran, New Zealand, and Sweden, the CDIAC database reported only the coal production category. For these cases, the brown coal in the Mitchell database was moved to the hard coal category, the CDIAC database was assumed to be correct, and the Mitchell data were adjusted.

Additional data sources covering shorter time periods were acquired from the Institute of Geological Sciences (1981, 1982) and the U.S. Bureau of Mines Statistical Yearbook (1986, 1993). For filling in data gaps, data from UN Statistical Yearbooks (1952, 1971, 1985) and the League of Nations (1936) were also utilized.

The consolidation and integration of the available production, import, and export data were accomplished as follows:

1. For the 1850-1950 period, the fuel production data were transferred from the Mitchell data sets.
2. For the 1950-1990 period, the CDIAC fuel data were used.
3. When the CDIAC data set had missing values, the data from Mitchell were used to fill in the period to 1975.
4. For Poland, a special data set reported by Jaros (1975) was used for the period 1850-1930.
5. Any remaining gaps in the fuels data (coal and oil) were linearly interpolated between the known time periods or the assumed onset of production. Extrapolations also were performed where appropriate.
6. For the 1850-1975 period, metal production data were transferred from the Mitchell data sets.
7. For the 1976-1980 period, metal data from the Institute of Geological Sciences/HMSO metal were used.
8. For the 1980-1990 period, metal data compiled by the U.S. Bureau of Mines were used.

It was decided not to interpolate the metal production data because of the small size of the effect.

Based on the above data sets, the production database is a homogeneous trend data set of 16 variables, (i.e., import and export for hard coal, brown coal, crude petroleum, and natural gas, as well as production data for the metals, copper, zinc, lead, and nickel).

As indicated previously, fossil fuels and most metal ores contain sizable concentrations of sulfur. During processing of fuels and metals, a fraction of sulfur is liberated into the atmosphere during combustion processes. The total mobilization rate of sulfur is determined by the production of fuels and metals, multiplied by their sulfur concentration. There is a sizable literature on the sulfur content of coals for various mining regions of the world. For hard and brown coal, the major coal sulfur content data sets were those in the World Energy Conference (1986) and World Energy Council (1992). Additional coal sulfur data were obtained from Kato (1996), Spiro *et al.* (1992), Husar (1986), Afinogenova and Ryaboshapko (1988), and Dianwu (1995). As an example, the coal sulfur content for 1970 is shown in Table 3 for hard coal and brown coal, respectively. The tables list literature values, as well as three sulfur content estimates used in this study, namely the minimum, maximum, and the "best" estimate for each country. The "best" estimate constitutes our recommended sulfur content for each country.

The sulfur content of oil is largely based on the data compiled by the Bartlesville Project Office (1987). The database contains the sulfur content of virtually all oil producing regions of the world. Table 3 summarizes the percent sulfur content for each country used in our study. The values were averaged for each country and the standard deviation among the values for each country was used to estimate the minimum and maximum for each country. When the standard deviation exceeded the mean, we assumed a standard deviation of 25%.

The Bartlesville Project Office provided information on the sulfur content of refined oil products in the United States for the period 1955-1990

for gas diesel, jet fuel, motor gas, residual oil, and kerosine. Because the CDIAC database contained production information on the above oil products, estimates of sulfur emissions reflect these products. Although we were unable to identify the sulfur content for all refined products in the CDIAC database, all of the above items were used, with an appropriate weighting for the missing refined products. The United States sulfur content for the refined products was used for all countries for the time period defined, except for Asia, where the data from Kato (1996) were used. We have assumed that the refining technology in practice defined the sulfur content of the refined products. Table 4 lists the percent sulfur in refined oil products for the United States from 1955 to 1990.

Detailed sulfur content for metals was not available for individual countries. For this reason, we adopted the emission factors from the EPA compilation of emission factors (U.S. EPA, 1995a). The emission factors are for uncontrolled emissions, without sulfur recovery. The emission factor is expressed as ton of sulfur per ton of the metal produced. For copper smelting, this factor is taken to be 1.2, for zinc 0.5, for lead 0.14, and for nickel 1.20. Also, we have assumed a 25% uncertainty for these emission factors.

The sulfur release factor represents the fraction of the sulfur in fuels and metals that is released to the atmosphere. Complete volatilization of sulfur during combustion yields a release factor of unity. In general, coal combustion in modern plants results in near complete volatilization of fuel sulfur. A small sulfur fraction is retained during coal preparation at the mines. Another fraction of the coal sulfur is retained in the fly ash. If flue gas desulfurization (FGD) is installed, then an additional fraction of

sulfur is removed as solid waste prior to atmospheric release and has been estimated using the information reported earlier. For oil products, the refining process tends to concentrate the sulfur in the heavy residues, such as residual fuel oil. Lighter refinery products, such as gasoline, are low in sulfur content, as indicated in Table 4. Metal smelting is also a refining process, where a fraction of the ore sulfur is recovered as a useful byproduct. Hence, the atmospheric release factor is well below unity for modern metal smelting. The sulfur release factors depend largely on the technologies used in the processing of fuels and metals. The sulfur release factor for individual countries of the world were not available for this study. Rather, we used charts of aggregate release factors that depict the historical trend of these factors since 1850. Several of these factors were developed by Darmstadter and Ayres (1987). The uncertainties of these factors are a major contributor to the uncertainty of sulfur emission estimates. This is particularly true for sulfur emission estimates associated with the oils and metals.

3. RESULTS AND DISCUSSION

3.1 Sulfur Production

The results are presented in trend charts that cover the period 1850-1990. As indicated in the Introduction, the emission estimates for each country in this study are based on the net production, percent sulfur, and sulfur retention information associated with a country's activities. We have assumed that net production is equated with consumption. The world coal production from 1850 to 1990 is depicted in Figure 2. This figure represents production and not "net production" and is therefore, not necessarily an

indication of consumption. The production of anthracite and bituminous hard coal exceeds brown coal production by approximately a factor of 3. The first growth of global coal production occurred between 1880 and 1910, followed by a plateau until about 1950. A second major rise is observed between 1950 and 1990. The production of world coal has doubled since 1950. Brown coal has become an increasing fraction of the total coal production. By 1990, hard coal and brown coal production was about 4.75 billion metric tons per year.

In 1900, the largest coal producing country was Great Britain, followed by the United States and Germany. In 1930, the United States coal production exceeded Great Britain by a substantial margin. By 1960, the three major coal producing countries were China, the United States, and the former U.S.S.R. This trend continued through 1990, when China became the largest coal producing country, followed by the United States and the former U.S.S.R. (Figure 3). The United States coal production shows a sharp rise around the turn of the century, followed by another increase after 1950. On the other hand, both the former U.S.S.R and China had low coal production prior to World War II, but exhibited a sharp rise in the post-war period. The most remarkable increase can be noted for China, which has increased its hard coal production from about 397 million metric tons during the 1960s to approximately 1.1 billion metric tons in 1990. The brown coal production in 1990 is most pronounced in Europe, most notably Germany and the former U.S.S.R. The global export and import of hard coal in 1990 accounted for about 10% of the global hard coal production, with the United States and Australia being the major exporters.

The world oil production shows an exponential growth from its onset about 1900 to the early 1970s (Figure 2). However, for the past twenty years,

the global production has fluctuated about 10%. The oil import and export indicate that prior to World War II, the international oil trade was insignificant. However, by the 1960s, the international flow of oil (i.e., export) had become about 50% of the global production.

The major oil producing countries in 1990 were the former U.S.S.R. (565,500,000 metric tons), the United States (369,679,000 metric tons), and Saudi Arabia (320,375,000 metric tons). Prior to World War II, the United States was the dominant oil producing nation. By 1970, both the former U.S.S.R and Saudi Arabia were equal to or exceeding the United States production. However, in the early 1980s, Saudi Arabia reduced its production below that of the United States.

It is also instructive to examine the net oil production over the world. The net production is defined as the sum of the physical production, plus the imports, minus the exports. In effect, the net production represents the oil consumption rate in a given country. Since the turn of the century, the United States has been the largest oil consumer; since about 1910, the consumption rate has been linearly increasing. The abrupt reduction of oil consumption in the 1970s was followed by an increase in the middle 1980s and a slight decrease in the late 1980s. The next major consumer, the former U.S.S.R., showed a sharp rise between 1950 and 1980, but modest change over the past decade. Japan shows little oil consumption prior to 1950, but an exponential growth up to 1970, followed by a slow decay period. For 1990, the major oil consumers are the United States (659,261,000 metric tons), the former U.S.S.R. (465,000,000 metric tons), China (109,360,000 metric tons), and Japan (190,225,000 metric tons), as well as the western European countries.

The world production of sulfur containing metals (copper, zinc, lead, and nickel) exhibits a rather varied behavior since 1850 (Figure 4). Copper, zinc, and lead have roughly comparable production rates from 1850 to about 1950. From 1950 on, the copper and zinc production have been increasing by a factor of 3-4, while the lead production has only doubled between 1950-1990. Between 1970 and 1990, the global lead production declined. Nickel production has steadily increased from 1930 to 1990 but at much lower magnitude than the other three metals. Table 5 describes the top 75% of the producers of the sulfur-containing metals copper, zinc, lead, and nickel for 1990. In 1990, the former U.S.S.R. and Canada were the major nickel producers.

The spatial pattern of world copper production for 1990 shows Chile, the United States, and Canada as the most prolific producers. A substantial copper production is also noted in Asia and Africa. During the first half of the century, copper production in the United States prevailed. However, since the 1980s, Chile has become a leading copper producer.

Canada, the former U.S.S.R., and Australia are the dominant producers of zinc, along with China, the United States, and Peru. The leading zinc producers had moderate production prior to World War II. However, since the 1950s, there has been a factor of 3-4 increase. In 1990, the major producers of zinc were Canada, Australia, the former U.S.S.R., China, Peru, and the United States.

The major lead producing nations in 1990 were Australia, the United States, and the former U.S.S.R. China, Canada, Peru, and Mexico were also significant lead producers. Prior to World War II, the United States lead production was the largest among the nations. However, since 1950, both Australia and the former U.S.S.R. have become the major lead producers.

3.2 Sulfur Emissions

The range of estimated global sulfur emissions by year is illustrated in Figure 5. The estimates derived from this study are identified by the curves denoted as "ASL/CAPITA." The average estimate of sulfur emissions was affected by the percent sulfur estimates provided by the World Energy Conference (1986) and World Energy Council (1992). The percent sulfur was identified in these publications as an average with a range, which defined our high and low estimates. The average estimates are considered the "best" estimates and are used for purposes of comparisons. All estimates of sulfur emissions are reported in metric tons of sulfur. To convert to sulfur dioxide (SO_2), the sulfur estimates should be multiplied by 2; to convert to short tons, the metric tons should be multiplied by approximately a factor of 1.1.

The global anthropogenic sulfur emission trend for 1850-1990 shows that there has been a general increase of sulfur emissions since 1850 (Figure 5). According to our estimates, the sulfur emissions in 1850 (approximately 1.2 million metric tons S) were about 1.7% of the current values (71.5 million metric tons S). Hence, 1850 appears to be a proper choice for the beginning of the emission trend analysis. As observed in the figure, beginning in 1913, there was a leveling off and some decline of sulfur emissions during World War I. From 1930-1932, serious decreases in global sulfur emissions occurred that apparently were associated with the Great Depression. From 1933 through 1944, emissions tended to increase, due in part to activities associated with World War II. However, in 1945, at the end of World War II, there was a sudden drop in sulfur emissions. From 1946 through the present time, global sulfur emissions have tended to rise. The drop in the 1981-1983 period is primarily

the result of the declining oil demand during the global recession.

Figures 6-12 illustrate the global sulfur emissions by region of the world.

Before describing further the results of the ASL/CAPITA sulfur emission estimates, it is important to compare the results of this study with the sulfur emissions estimates made by others. Möller (1984) estimated the global anthropogenic sulfur emissions from 1860 to 2000. The author estimated global sulfur emissions from 1860 to 2000 using mean emission factors. Although a consistent methodology was used, average emission factors were used instead of country- or source-specific information. Similarly, Dignon and Hameed (1989) used statistical models that relate the rate of emissions of sulfur dioxide to the rate of fuel consumption to estimate global emissions at 10-year intervals from 1860 to 1980. Figure 13 shows a comparison of the global emissions by Möller (1984), Dignon and Hameed (1989), and this study (ASL/CAPITA) for 10-year increments. In all cases, the estimates reported by Möller (1984) were higher than the other two. The sulfur estimates, using only fossil fuel, by Dignon and Hameed (1989) agreed closely with ASL/CAPITA estimates. If the sulfur emissions associated with metal production had been included by Dignon and Hameed (1989), these values would have exceeded the estimates of this study.

Other investigators have estimated global sulfur emissions for shorter time periods (e.g., Spiro et al., 1992; Benkovitz et al., 1996). The method used by Spiro et al. (1992) was applied originally to all countries. However, for the United States, Spiro et al. (1992) reported an overestimate of sulfur emissions by a factor of 1.8. The authors reported that their estimates for North America, Europe, and eastern Asia were overwritten with existing inventories. Thus, the authors were unable to apply their methodology across

all countries to estimate global sulfur emissions. Figure 14 illustrates the comparison between the sulfur emission estimates of this study and those of Benkovitz *et al.* (1996), Spiro *et al.* (1992), and Dignon and Hameed (1989). For 1980, the values reported by Spiro *et al.* (1992) were higher than those reported in this study and Dignon and Hameed (1989). The values reported for 1985 by Benkovitz *et al.* (1996) were almost identical to the values estimated in this study (i.e., approximately 65 million metric tons). Similarly, for 1990, the estimates by ASL/CAPITA and those by Benkovitz *et al.* (1996) were approximately 71.5 million metric tons. As indicated earlier, Benkovitz *et al.* (1996) used an entirely different protocol for estimating global sulfur emissions than the protocol followed in this study.

Estimates of sulfur emissions in Europe have been made for 1985 and 1990 (Mylona, 1993; Benkovitz *et al.*, 1996; U.S. EPA, 1995b). The Environmental Protection Agency (U.S. EPA, 1995b) has published sulfur emission estimates for countries in Europe. As part of the European program CORINE (COoRdination d'INformation Environnementale), the CORINE AIR emission inventory (CORINAIR) for 1985 and 1990 has been published by the EPA. Figures 15 and 16 illustrate the comparisons of the estimates from ASL/CAPITA, Mylona (1993), CORINAIR (U.S. EPA, 1995b), and Benkovitz *et al.* (1996). In general, except for a few countries (e.g., West Germany and Italy), the European estimates from this study compared favorably with those of others. Figure 17 illustrates the comparison between the estimates made by Mylona (1993) and ASL/CAPITA for the former U.S.S.R. Differences are clearly evident between the two approaches for the period 1950 to 1990. Benkovitz *et al.* (1996) estimated 12.3 and 12.6 million metric tons for 1985 and 1990, respectively, while the ASL/CAPITA estimates were 11.5 and 10.9 million metric tons, based on the production,

import, and export information. Mylona (1993) estimated sulfur emissions to be 12.7 and 13.7 million metric tons for the same periods. Figure 18 shows that the Kato (1996) estimates for Japan were in the range of 37-66% of the sulfur emission estimates made by ASL/CAPITA. As indicated earlier, some of the sulfur content data for coal and oil refining products for Asia were taken from Kato (1996). In addition, this study has taken into consideration the use of FGD in reducing the emissions associated with coal burning. Thus, assuming that the production figures we obtained from CDIAC and Mitchell are similar to the values used by Kato (1996), we assume that the differences in emission estimates may be associated with activities removing sulfur from coal (e.g., coal washing) not included in our approach. Figure 19 shows a comparison of the sulfur emission estimates made by Kato and Akimoto (1992), Benkovitz et al. (1996), and ASL/CAPITA for Asia for 1985. Because the estimates made by Benkovitz et al. (1996) for several of the countries in Asia included estimates made by others as cited in the literature (including Kato and Akimoto (1992)), one would not necessarily expect differences between those of Benkovitz et al. (1996) and Kato and Akimoto (1992).

The U.S. EPA (1995b) summarized trends for the United States for the period 1900-1994. Figure 20 shows the comparison between the values published by the EPA and the estimates resulting from this study for 10-year increments. The EPA's estimates identify a downward trend of sulfur emissions in the United States from the mid-70s to 1990. Alternatively, the ASL/CAPITA analysis shows a leveling off of sulfur emissions from the mid-70's to early 80's, a downward trend until the mid-80's, and then a gradual increase into the 1990s. Benkovitz et al. (1996) reported an increase from 10.8 to 11 million metric tons of sulfur emissions for 1985 and 1990, respectively. For

1985 and 1990, the ASL/CAPITA sulfur estimates were 10.8 and 12.5 million metric tons, while the EPA estimated 10.6 and 10.2 million metric tons for 1985 and 1990, respectively. Thus, the discrepancy between (1) the U.S. EPA estimates and (2) those of this study and Benkovitz et al. (1996) appears to exist following 1985.

As described in Appendix A, the United States sulfur estimates made by Benkovitz et al. (1996) were taken from the U.S. EPA Interim Inventory for 1990. The Interim Inventories are compiled by the U.S. EPA with input from the EPA Regional Offices and individual states and are the values used for enforcement activities. The totals were obtained from the U.S. EPA files for point and area sources dated June 1993.

We have investigated possible causes for the discrepancy between the values reported in this study for the United States and the values reported by the U.S. EPA. Table 6 shows that the largest differences between the two estimates are for emissions associated with coal and oil. Some of the difference in the oil category may be associated with the consumption of residual fuel oil. For 1990, the U.S. EPA (1994) estimated some of the United States sulfur emissions based on growth projections and not necessarily the actual consumption experienced during a specific year. It was not possible to identify from EPA's data the number of metric tons of residual fuel oil estimated to be consumed. However, OECD (1973-1991) has reported that the United States consumed 54,160,000 metric tons in 1990. For our sulfur estimates, we used the CDIAC database, which for 1990, estimated the United States consumption at 52,346,000 metric tons of residual fuel oil. As noted in Table 4, residual fuel oil has much higher sulfur content than diesel, jet fuel, motor gas, and kerosine. Thus, some of the discrepancy between the

ASL/CAPITA sulfur emission estimates and those of the U.S. EPA may be associated with the differences in estimates for the residual fuel consumption; therefore the higher sulfur emissions estimated in the United States as a result of this study and as reported by Benkovitz *et al.* (1996) may be closer to the actual values for 1990.

For coal emissions, we reviewed the categories in which the U.S. EPA (1995b) reported its national emissions of sulfur. We believe that part of the inconsistency shown in Table 6 associated with coal emissions may be linked with the "other" category in this study's table. The U.S. EPA (1995b) lists several other source categories in its table that may be associated with coal combustion activities (e.g., other industrial processes, chemical and allied product manufacturing, metals processing, etc.). In addition, the U.S. EPA (1994) assumes that sulfur dioxide and PM-10 controls are 100 percent effective. As noted in Table 2, for 1990, this study used 85% as the average efficiency of sulfur removal for FGD controls. The 85% efficiency was calculated by averaging the sulfur removal efficiencies, weighted by the megawatts of electricity consumed, associated with the technologies used (IEA London, private communication). Thus, some of the discrepancy for the sulfur emissions related to the coal consumption sector between our study and those of the U.S. EPA may be associated with the level of FGD efficiencies used in the analyses.

Previously, we discussed the use of applying several approaches required for estimating sulfur emissions. Figure 21 shows the effect of applying various corrections to the database for estimating sulfur emissions in the United States. The figure shows the effects on sulfur emissions as a function of modifying oil retention by using the sulfur content of refined oil products

(i.e., gas diesel, jet fuel, motor gas, residual oil, and kerosine). Note that the effect of using FGD controls showed only a marginal decrease in sulfur emissions in the United States (Figure 21). On the other hand, the use of low-sulfur coals in combustion appears to have had a greater effect on sulfur emission reductions in the United States than the FGD controls. As indicated in Figure 1, from 1973 through 1990, the average percent of sulfur in coal used for combustion purposes in the United States decreased from approximately 2.3% to 1.3% and its effect on emissions is illustrated in Figure 21. On a global scale, similar observations are found when evaluating global sulfur emissions (Figure 22). However, it must be noted that for a specific country (e.g., western Germany), FGD controls may have a major impact on its nation's sulfur emissions.

The spatial pattern of global sulfur emissions (Figure 23) shows that the United States, the former U.S.S.R., and China were the main sulfur emitters (i.e., approximately 50% of the total emissions) in the world in 1990. Note that although the former U.S.S.R. and the United States appear to have stabilized their sulfur emissions over the past 20 years, the recent increase in global sulfur emissions appears to be linked to the rapid increases associated with sulfur emissions in mainland China. Figure 24 shows the temporal sulfur emissions for the three major emitters. For 1990, the top three sulfur-emitting countries account for 53% of the global sulfur emissions.

Combustion of anthracite and bituminous hard and brown coal is the dominant source of anthropogenic sulfur emissions. The contribution of oil products rose rapidly between 1950 and 1980 (Figure 25). However, these rapid increases have not continued. Similarly, sulfur emissions associated with

copper smelting peaked in 1974 (Figure 26). Therefore, the steady increase of global sulfur emissions since the 1970s is attributable to increases in coal combustion. The sulfur emission trends associated with the combustion of anthracite and bituminous hard coal are mainly due to the United States, China, and the former U.S.S.R. However, historical trends of sulfur emissions for the above three countries are remarkably different (Figure 27). While the United States shows substantial emissions associated with these fuels prior to 1940, China and the former U.S.S.R. show virtually no emissions in the first half of the century. Sulfur emissions from brown coal occur mainly over Europe. The former U.S.S.R., Yugoslavia, and Germany show substantial increases since 1940, but not significant emissions prior to World War II.

The major sulfur emitters from oil consumption are the United States, the former U.S.S.R., and Saudi Arabia, with notable emissions from Mexico, China, and Japan. The historical trends of oil sulfur emissions for the major emitters, the United States, U.S.S.R., and Saudi Arabia, show the early dominance of the United States and the subsequent emergence of the other two countries since the 1950s (Figure 28).

The sulfur emissions from copper show an identical pattern to the copper production, since both sulfur content of ores and the atmospheric emission fraction were assumed to be geographically constant. Since 1910, the sulfur emission trends for the United States show highly fluctuating values. On the other hand, since 1920, Chile shows a steady increase of copper-related emissions. In 1990, the major sulfur emitters from copper production were Chile (911,400 metric tons), the United States (673,600 metric tons), Canada (452,300 metric tons), the former U.S.S.R. (338,400 metric tons), Zambia (292,700 metric tons), Zaire (232,900 metric tons), and Poland (208,700 metric

tons). Canada (117,600 metric tons), Australia (93,700 metric tons), the former U.S.S.R. (75,000 metric tons), and China (61,900 metric tons) produce the major zinc-related sulfur emissions. The lead-related sulfur emission rate in 1990 was highest in Australia (39,700 metric tons), the United States (35,000 metric tons), the former U.S.S.R (28,200 metric tons), China (22,200 metric tons), and Canada (16,400 metric tons). The sulfur emissions associated with nickel production is dominated by the former U.S.S.R. (146,600 metric tons) and Canada (112,200 metric tons).

4. CONCLUSIONS

The ASL/CAPITA database describing, spatially and temporally, production information, percentage of sulfur in fuels and metals, retention factors based on technological removal of sulfur, and sulfur emissions, has been developed for the period 1850 to 1990. Special effort was devoted to ensuring that a common methodology was applied across all years and countries for the estimation of emissions. The use of a consistent methodology makes it possible to produce global totals by adding estimates from each country. The current protocol for deriving sulfur emission estimates generally compares favorably with previously-applied methods. Yearly temporal resolution information is available from the database; changes associated with specific historical events (e.g., wars, depressions, etc.) are clearly observed in the emission inventory on a national, regional, or global basis.

On a global basis for extended periods, the sulfur estimates, using only fossil fuel, by Dignon and Hameed (1989) agreed almost exactly with the ASL/CAPITA estimates. The values reported for 1985 by Benkovitz et al. (1996) were almost identical to the values estimated in this study (i.e.,

approximately 65 million metric tons). Similarly, for 1990, the estimates by ASL/CAPITA and those by Benkovitz *et al.* (1996) were approximately 71.5 million metric tons. Benkovitz *et al.* (1996) used an entirely different protocol for estimating global sulfur emissions than the protocol followed in this study. In general, except for a few countries (e.g., West Germany and Italy), the European estimates from this study compared favorably with those of Mylona (1993), CORINAIR (U.S. EPA, 1995b), and Benkovitz *et al.* (1996). However, some discrepancies were found. For example, the Kato (1996) estimates for Japan were in the range of 37-66% of the sulfur emission estimates made by this study. In addition, the U.S. EPA (1995b) estimates identified a downward trend of sulfur emissions in the United States from the mid-70s to 1990. On the other hand, this study shows a leveling off of sulfur emissions from the mid-70's to early 80's, a downward trend until the mid-80's, and then a gradual increase into the 1990s. Upon closer investigation, we believe that some of the discrepancy between the ASL/CAPITA sulfur emission estimates and those of the U.S. EPA's may be associated with differences in estimates for the residual fuel consumption. In addition, the U.S. EPA (1994) assumes that sulfur dioxide and PM-10 controls are 100 percent effective. For 1990, this study used 85% as the average efficiency of sulfur removal for FGD controls, based on the data received from the IEA (private communication). Therefore, the higher sulfur emissions estimated for the United States as a result of this study and those reported by Benkovitz *et al.* (1996) may be closer to the actual values for 1990.

We investigated the possible contribution of several reduction sulfur emission options. In our study, it appears that using FGD controls showed only a marginal decrease in sulfur emissions in the United States. On the

other hand, in the United States, the use of low-sulfur coals in combustion appears to have had a greater effect on sulfur emission reductions in the United States than the FGD controls. From 1973 through 1990, the average percent of sulfur in coal used for combustion purposes in the United States has decreased substantially and its effect on emissions was clearly observed. On a global scale, similar observations are found when evaluating global sulfur emissions. However, it must be noted that for a specific country, FGD controls have a major impact on its nation's sulfur emissions.

The spatial pattern of global sulfur emissions shows that the United States, the former U.S.S.R., and China were the main sulfur emitters (i.e., approximately 50% of the total emissions) in the world in 1990. For 1990, the top three sulfur-emitting countries account for 53% of the global sulfur emissions. Combustion of anthracite and bituminous hard and brown coal is the dominant source of anthropogenic sulfur emissions. The sulfur emission trends associated with the combustion of hard coal are mainly due to the United States, China, and the former U.S.S.R. However, historical trends of sulfur emissions for the above three countries are remarkably different. While the United States shows substantial emissions prior to 1940, China and the former U.S.S.R. show virtually no emissions in the first half of the century; however, these two countries contributed greatly to the sulfur emissions in the latter half of this century. Although sulfur emissions appear to have stabilized over the past 20 years in the former U.S.S.R. and the United States, the recent increase in global sulfur emissions appears to be linked to the rapid increases associated with sulfur emissions in mainland China.

Krug, in Appendix B, points out that there is a large range of estimates for natural sulfur emissions to the atmosphere. Marine sulfur emissions are

significant and have a large (i.e., 5-fold, > 40 million metric tons per year) range in reported values. A model developed to predict the effect of anthropogenic marine eutrophication on marine sulfur gas emissions shows that current levels of marine eutrophication do not significantly affect marine S gas emissions. Krug points out that volcanic activity is a significant natural source of sulfur emission. The wide range in reported values appears to be due to large variations in volcanic activity, as well as to assumptions used in modeling. In Appendix C, Benkovitz *et al.* estimate the total sulfur emitted by volcanic activity in 1985 to be 14.5 million metric tons sulfur from 41 active volcanoes. For 1990, Benkovitz *et al.* estimate the total sulfur emitted by volcanic activity at 11.6 million metric tons sulfur from 44 active volcanoes.

Wind-blown soil (aeolian activity) is an appreciable natural sulfur source to the atmosphere. However, the flux of aeolian sulfur is principally limited to certain arid and semi-arid regions, particularly interior Asia and Australia, where erodible gypsumiferous soils are common. Finally, estimates of annual flux of sulfur emissions from biomass burning (i.e., fire) are ≥ 2 million metric tons sulfur per year. Estimates of sulfur gas emissions from terrestrial biomass show such emissions to be small compared to other natural emission sources.

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Table 1. Cumulative total of FGD capacity by year. Units in MW.

COUNTRY	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
AUSTRIA										1.4	1.3	1.3	9.3	27.9	25.8	25.4	26.7	27.0
CANADA												0.0	0.0	0.0	0.0	0.0	0.0	1.0
DENMARK																	7.0	13.7
FINLAND																3.6	5.3	5.0
FRANCE													2.2	2.4	2.5	2.6	2.6	2.6
W. GERMANY										1.9	1.9	1.9	4.3	9.6	23.4	40.5	43.3	43.2
INDIA																1.1	1.0	0.9
ITALY															0.2	0.2	0.2	0.3
JAPAN	0.2	0.2	0.7	1.6	1.8	1.8	1.9	2.0	2.9	3.2	5.5	6.7	7.6	8.1	8.5	8.4	8.8	9.2
NETHERLANDS															3.2	16.4	16.6	16.5
RUSSIAN FED.																		0.1
SWEDEN										1.0	2.4	2.4	5.3	9.5	9.9	10.0	10.0	9.2
SWITZERLAND																	10.1	10.0
TURKEY																0.4	0.4	0.4
USA	0.3	0.4	0.8	1.1	2.1	3.4	4.8	6.0	6.6	7.8	9.0	9.6	11.3	12.3	12.9	13.2	13.3	13.4

Table 2. The average efficiency of FGD controls by year.

COUNTRY	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
AUSTRIA										55.0	55.0	55.0	85.2	92.7	90.7	90.7	90.7	90.7
CANADA												30.0	30.0	30.0	30.0	30.0	30.0	74.1
DENMARK																	91.2	91.2
FINLAND																80.0	83.5	83.5
FRANCE													60.0	60.0	60.0	60.0	60.0	60.0
W. GERMANY									85.0	90.0	90.0	90.0	89.8	90.8	91.8	90.5	90.6	90.6
INDIA																85.0	85.0	85.0
ITALY															81.0	81.0	81.0	84.9
JAPAN	90.0	90.0	90.7	90.3	90.1	90.1	89.8	88.6	90.4	90.5	89.8	89.6	89.6	89.8	90.0	90.0	90.0	89.9
NETHERLANDS															88.0	88.8	88.8	88.8
RUSSIAN FED.																		75.0
SWEDEN										90.0	75.3	75.3	72.9	75.8	75.8	75.8	75.8	75.8
SWITZERLAND																	90.0	90.0
TURKEY																92.0	92.0	92.0
USA	80.3	81.9	83.1	78.3	79.2	80.6	82.2	82.4	82.5	83.8	84.1	84.4	84.9	85.1	85.3	85.4	85.2	85.0

Table 3. The resulting sulfur content in hard coal, brown coal, and crude oil as used in this study. The percentages for hard and brown coal are for 1970.

Country	Hard Coal			Brown Coal			Crude Oil		
	Best	Max	Min	Best	Max	Min	Best	Max	Min
AFGHANISTAN	0.50%	0.63%	0.42%	0.50%	0.63%	0.40%			
AFRICA SOUTH	0.84%	1.02%	0.60%	0.84%	1.05%	0.67%			
ALBANIA							4.85%	5.91%	3.80%
ALGERIA							0.11%	0.19%	0.03%
AMERICA, UNITED STATES	2.02%	2.42%	1.62%	0.92%	1.15%	0.70%	0.70%	0.86%	0.52%
ARGENTINA	0.80%	1.00%	0.67%	0.80%	1.00%	0.64%	0.13%	0.28%	0.13%
AUSTRALIA	0.50%	1.10%	0.50%	0.50%	2.20%	0.40%	0.13%	0.19%	0.06%
AUSTRIA	1.05%	1.32%	0.88%	1.05%	1.31%	0.84%	1.10%	1.37%	0.82%
BAHRAIN							1.78%	1.93%	1.27%
BANGLADESH	0.62%	0.78%	0.52%						
BELGIUM	0.90%	1.13%	0.75%	0.90%	1.13%	0.72%			
BRAZIL	2.50%	3.14%	2.09%	2.50%	3.13%	2.00%			
BRUNEI	0.62%	0.78%	0.52%	0.62%	0.77%	0.50%			
BULGARIA	0.70%	0.88%	0.59%	0.70%	0.88%	0.56%			
BURMA (MYANMAR)	0.86%	1.08%	0.72%	0.86%	1.08%	0.69%	0.13%	0.18%	0.09%
CANADA	1.20%	1.51%	1.00%	0.50%	0.63%	0.40%	1.21%	1.81%	0.60%
CHILE	2.00%	2.51%	1.67%	2.00%	2.50%	1.60%	1.15%	1.60%	0.72%
CHINA (MAINLAND)	1.35%	1.60%	1.16%	1.35%	1.60%	1.16%	0.88%	1.10%	0.66%
COLOMBIA	0.90%	1.13%	0.75%	1.20%	1.55%	0.96%	0.88%	1.43%	0.34%
CUBA							1.68%	2.43%	0.94%
CZECHOSLOVAKIA	0.65%	0.82%	0.54%	1.80%	2.25%	1.40%	1.30%	1.62%	0.98%
ECUADOR							0.77%	0.96%	0.58%
EGYPT							2.18%	3.35%	1.01%
FRANCE	0.90%	1.13%	0.75%	1.50%	1.88%	1.20%	1.02%	1.53%	0.51%
GABON							0.55%	0.80%	0.31%
GERMANY, DEMOCRATIC REPUBLIC	1.00%	1.25%	0.84%	0.60%	0.90%	0.48%			
GERMANY, FEDERAL REPUBLIC	1.00%	1.10%	1.00%	0.60%	1.40%	0.48%			
GERMANY, UNIFIED	1.00%	1.25%	0.84%	0.60%	0.75%	0.48%			
GREECE	1.00%	1.25%	0.84%	1.00%	1.25%	0.80%	3.06%	3.82%	2.29%
HONG KONG	0.53%	0.67%	0.44%	0.53%	0.66%	0.42%			
HUNGARY	2.50%	3.14%	2.09%	2.90%	3.10%	2.32%			
INDIA	1.00%	2.30%	0.63%	1.00%	1.40%	0.94%	0.11%	0.13%	0.09%
INDONESIA	0.29%	0.36%	0.24%	0.29%	0.36%	0.23%	0.18%	0.03%	0.03%
IRAN							1.68%	2.41%	0.96%
IRAQ							1.95%	1.98%	1.92%
IRELAND	1.25%	1.57%	1.04%	1.25%	1.56%	1.00%			
ISRAEL							2.51%	3.77%	1.26%
ITALY	0.70%	0.88%	0.59%	0.70%	0.88%	0.56%	0.10%	0.10%	0.10%

Table 3. (continued).

Country	Hard Coal			Brown Coal			Crude Oil		
	Best	Max	Min	Best	Max	Min	Best	Max	Min
JAPAN	0.67%	0.84%	0.50%	1.01%	1.26%	0.75%	0.45%	0.75%	0.15%
KOREA, NORTH	0.32%	0.40%	0.27%	0.48%	0.60%	0.38%			
KOREA, SOUTH	0.70%	0.88%	0.59%	0.74%	0.93%	0.59%			
KUWAIT						2.57%	3.18%	1.96%	
LAO PEOPLES DEMOCRATIC	0.62%	0.78%	0.52%	0.62%	0.77%	0.50%			
LIBYAN ARAB JAMAH							0.43%	0.77%	0.09%
MALAYA-SINGAPORE	0.57%	0.72%	0.48%	0.93%	1.16%	0.74%			
MALAYSIA	0.57%	0.72%	0.48%	0.16%	0.20%	0.13%			
MALDIVES	0.62%	0.78%	0.52%						
MEXICO	1.00%	1.25%	0.84%	0.80%	1.00%	0.64%	3.21%	4.88%	1.54%
MONGOLIA	0.70%	0.88%	0.59%	0.70%	0.88%	0.56%			
MOROCCO	2.00%	2.51%	1.67%	2.00%	2.50%	1.60%	0.10%	0.12%	0.08%
NIGERIA							0.19%	0.36%	0.02%
NEPAL	0.62%	0.78%	0.52%						
NETHERLANDS							0.74%	1.05%	0.44%
NEW ZEALAND	1.22%	1.53%	1.02%	0.36%	0.45%	0.29%	0.10%	0.12%	0.08%
NORWAY	0.97%	1.22%	0.81%	0.97%	1.21%	0.78%	0.16%	0.22%	0.11%
PAKISTAN (72-)	3.65%	4.58%	3.05%	3.65%	4.56%	2.92%	0.32%	0.40%	0.24%
PAKISTAN, EAST & WEST	3.65%	4.58%	3.05%	3.65%	4.56%	2.92%			
PENINSULAR MALAYSIA	0.57%	0.72%	0.48%	0.16%	0.20%	0.13%			
PERU							1.00%	1.25%	0.75%
PHILIPPINES	1.30%	1.63%	1.09%	1.30%	1.62%	1.04%			
POLAND	0.95%	0.95%	0.74%	0.50%	1.10%	0.40%			
PORTUGAL	1.25%	1.57%	1.04%	1.25%	1.56%	1.00%			
QATAR							1.67%	1.95%	0.79%
ROMANIA	2.00%	2.51%	1.67%	3.00%	3.75%	0.70%	0.20%	0.27%	0.13%
SABAH				0.16%	0.20%	0.13%			
SARAWAK	0.57%	0.72%	0.48%	0.16%	0.20%	0.13%			
SAUDI ARABIA							2.13%	2.67%	1.60%
SERBIA				2.40%	3.00%	1.92%			
SINGAPORE	0.62%	0.78%	0.52%	0.62%	0.77%	0.50%			
SPAIN	0.50%	0.63%	0.42%	2.00%	2.50%	1.60%			
SRI LANKA	0.66%	0.83%	0.55%	0.66%	0.82%	0.53%			
SWEDEN	0.45%	0.56%	0.38%	0.45%	0.56%	0.36%			
TAIWAN	1.67%	2.10%	1.40%	2.82%	3.53%	2.26%			
THAILAND	2.11%	2.64%	1.76%	1.60%	2.36%	1.28%			

Table 3. (continued).

Country	Hard Coal			Brown Coal			Crude Oil		
	Best	Max	Min	Best	Max	Min	Best	Max	Min
TURKEY	2.80%	3.51%	2.34%	2.80%	3.30%	2.00%			
UNITED ARAB EMIRATES							0.71%	0.77%	0.65%
UNITED KINGDOM	1.66%	1.73%	1.40%	1.66%	2.07%	1.33%	0.23%	0.37%	0.09%
USSR	1.44%	1.80%	1.33%	1.44%	1.44%	0.70%	0.80%	1.20%	0.40%
VENEZUELA	0.66%	0.83%	0.55%	0.66%	0.82%	0.53%	1.60%	2.80%	0.40%
VIET NAM (70 -)	0.20%	0.25%	0.17%	0.20%	0.25%	0.16%			
YUGOSLAVIA	2.40%	3.01%	2.01%	2.40%	3.00%	1.92%	1.30%	1.40%	1.20%
ZAMBIA (64 -)	1.59%	2.00%	1.33%	1.59%	1.99%	1.27%			
OTHER COUNTRIES	1.40%	1.75%	1.17%	1.18%	1.55%	0.81%	1.15%	1.60%	0.72%

Table 4. Percent sulfur in refined oil products for the United States from 1955 to 1990.

OIL PRODUCT	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966
GAS DIESEL REFINE	0.336	0.375	0.298	0.306	0.284	0.269	0.218	0.237	0.292	0.250	0.233	0.220
JET FUEL REFINE	0.116	0.137	0.088	0.048	0.057	0.040	0.051	0.044	0.055	0.052	0.059	0.066
MOTOR GAS REFINE	0.076	0.070	0.062	0.057	0.055	0.053	0.049	0.048	0.044	0.044	0.044	0.040
RESIDUAL FUEL REFINE	1.696	1.592	1.546	1.568	1.634	1.666	1.664	1.610	1.628	1.672	1.606	1.750
KEROSINE	0.116	0.137	0.088	0.048	0.057	0.040	0.051	0.044	0.055	0.052	0.059	0.066
OIL PRODUCT	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978
GAS DIESEL REFINE	0.227	0.259	0.228	0.271	0.248	0.210	0.235	0.267	0.319	0.256	0.272	0.267
JET FUEL REFINE	0.064	0.065	0.052	0.049	0.045	0.048	0.045	0.054	0.054	0.060	0.061	0.053
MOTOR GAS REFINE	0.042	0.037	0.037	0.037	0.038	0.038	0.036	0.036	0.034	0.028	0.029	0.026
RESIDUAL FUEL REFINE	1.700	1.704	1.810	1.760	1.670	1.710	1.604	1.638	1.540	1.502	1.592	1.480
KEROSINE	0.064	0.065	0.052	0.049	0.045	0.048	0.045	0.054	0.054	0.060	0.061	0.053
OIL PRODUCT	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
GAS DIESEL REFINE	0.236	0.254	0.278	0.280	0.288	0.280	0.260	0.266	0.279	0.258	0.259	0.268
JET FUEL REFINE	0.050	0.053	0.057	0.054	0.051	0.057	0.055	0.035	0.052	0.054	0.048	0.047
MOTOR GAS REFINE	0.028	0.028	0.031	0.030	0.025	0.033	0.031	0.033	0.031	0.029	0.031	0.032
RESIDUAL FUEL REFINE	1.468	1.614	1.590	1.560	1.364	1.546	1.618	1.643	1.817	1.817	2.740	2.765
KEROSINE	0.050	0.053	0.057	0.054	0.051	0.057	0.055	0.035	0.052	0.054	0.048	0.047

Table 5. The top 75% of the producers of the sulfur-containing metals copper, zinc, lead, and nickel for 1990. Units are 1000 metric tons.

Country	Amount Produced	Country	Amount Produced
Copper		Zinc	
Chile	1616	Canada	1176
United States	1194	Australia	937
Canada	802	Former USSR	750
Former USSR	600	China (Mainland)	619
Zambia	519	Peru	577
Zaire	413	United States	543
Poland	370	Belgium	357
Peru	318	Mexico	322
Australia	316	Spain	258
		North Korea	230
Lead		Nickel	
Australia	563	Former USSR	260
United States	497	Canada	199
Former USSR	400	Indonesia	68
China (Mainland)	315	Australia	67
Canada	232	Cuba	40
Peru	189	China (Mainland)	33
Mexico	180	Dominican Republic	29
Former Yugoslavia	99		

Table 6. Comparison of ASL/CAPITA United States sulfur emission estimates for 1990 with those of the U.S. EPA (1995b). Units are 1000 metric tons of S.

	Coal	Oil	Gas	Metals	Other	Total
ASL/CAPITA	9573	2179	0	764	0	12,516
U.S. EPA	7836	831	160	301	1348	10,175

Average Percent Sulfur in Coal Received at Electric Utilities in the United States by Year

Sources: Energy Information Administration (1981, 1986, 1991) for 1977-1990
U.S. Department of Energy (private communication) for 1973-1976

Figure 1

Comparison of Global Production of Anthracite and Bituminous Hard Coal, Brown Coal, and Oil

Figure 2

Comparison of Anthracite and Bituminous Hard Coal Production of Former USSR, China, and USA

Figure 3

Comparison of Global Production of Copper, Lead, Zinc, and Nickel

Figure 4

Range of Estimated Global Sulfur Emissions ASL/CAPITA

Figure 5

Sulfur Emissions in North America

Figure 6

Sulfur Emissions (1000 Metric Tons)

Sulfur Emissions in Europe

YEAR

Figure 7

Figure 8

Sulfur Emissions (1000 Metric Tons)

Sulfur Emissions in South America

Figure 9

Sulfur Emissions in Central America

Figure 10

Sulfur Emissions in the Middle East

Figure 11

Figure 12

Comparison of Global Sulfur Emissions

Figure 13

A Comparison of ASL/CAPITA and Other Global Sulfur Emission Estimates

Figure 14

Comparison of Estimates of European Sulfur Emissions 1985

Figure 15

Comparison of Estimates of European Sulfur Emissions 1990

Figure 16

Comparison of Estimates of Former USSR Sulfur Emissions

Figure 17

Comparison of Estimates of Sulfur Emissions in Japan

Figure 18

Comparison of Sulfur Emission Estimates for Asia 1985

Figure 19

Comparison of U.S. Sulfur Emissions

Figure 20

The Effect of Applying Various Corrections to the Database United States (1850-1990)

Figure 21

The Effect of Applying Various Corrections to the Database Global Estimates (1850-1990)

Figure 22

Change in Major Sulfur Emitters in Comparison to Remainder of the World

Figure 23

Comparison of Sulfur Emissions of Former USSR, China, and USA

Figure 24

**Global Sulfur Emissions Associated with
Net Anthracite and Bituminous Hard
Coal, Brown Coal, and Oil**

Figure 25

Global Sulfur Emissions Associated with Copper, Lead, Nickel, and Zinc

Figure 26

Sulfur Emissions Associated with Net Anthracite and Bituminous Hard Coal for the 3 Major Emitters

Figure 27

Sulfur Emissions Associated with Oil Production for the 3 Major Emitters

Figure 28

APPENDIX A

Global Anthropogenic Sulfur Emissions for 1985 and 1990

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A.1. INTRODUCTION

For the last several decades the combustion of fossil fuels has been the major source of anthropogenic emissions of oxides of sulfur (SO_x) to the atmosphere (Cullis and Hirschler, 1980, Logan, 1983, Saeger, *et al.*, 1989, Várhelyi, 1985, Wagner, *et al.*, 1986). Coal combustion, especially in large electric and heat power plants, and combustion of residential fuel oil are responsible for most of the emissions.

The sulfur content of fuels, especially in coal, is a major factor affecting SO_x emissions. This content is extremely variable, ranging from less than 1% to about 9%. On average, from 5 to 15% of the sulfur in fuels used in electric and heat generating power plants is retained in bottom and fly ashes. Various types of flue gas desulfurization (FGD) control devices are used to remove SO_x from the exhaust gases, predominantly in power plants in the United States, Canada, Western Europe, Japan and Australia. Crude petroleum is also extremely variable in the sulfur content, ranging from 0.3 to 2%, depending on the location of the petroleum field. In the refining process, most of the sulfur in the crude oil may be recovered; what is not

recovered remains mainly in the residual oil fraction. The processing of sulfur-containing materials (e.g., roasting of ores, sintering plants, etc.), the production of sulfur compounds (e.g., sulfuric acid manufacturing), and the use of sulfur compounds to produce other industrial goods (e.g., cellulose production) generate large amounts of SO_x . Although most of this sulfur may be recovered, not all installations do so; the sulfur that is not recovered is released to the atmosphere.

A.2. GLOBAL ANTHROPOGENIC SULFUR EMISSIONS IN 1985

A global inventory of SO_x emissions from anthropogenic sources for circa 1985 was compiled by an international group under the umbrella of the Global Emissions Inventory Activity (Benkovitz and Graedel, 1992) of the International Global Atmospheric Chemistry Programme (Galbally, 1989). In order to make the inventory useful for modeling atmospheric transport, transformation and removal the emissions were allocated to a $1^\circ \times 1^\circ$ longitude/latitude grid. A gridded global "default" inventory was selected and more accurate gridded and updated regional and national inventories and surrogate information were evaluated and used if appropriate. The regional inventories used include the regional inventories for the United States and Canada to 60°N compiled by the National Acid Precipitation Assessment Program (NAPAP) (Saeger, et al., 1989), EMEP and CORINAIR85 for Europe (Bouscaren, 1992, Sandnes and Styve, 1992), Kato and Akimoto (1992) and Tonooka (personal communication, 1993) for Asia, Carnovale (1992, Horseman and Carnovale, 1989) for Australia, and Loyd (personal communication, 1993) for South Africa. SO_x emissions for other regions of the globe were taken from a "default" inventory which was based on the work by Spiro et al. (1992) updated to 1985. Diagrams

of the relationship between the default inventories and the regional inventories used are presented in Figure 1. The work and results are described in Benkovitz et al. (1996); the resulting inventory has been designated Version 1A and is intended to serve as a basis for modeling and related activities by the international scientific community.

Global population density maps for 1985 were prepared on a $1^\circ \times 1^\circ$ longitude/latitude grid by Logan (J. Logan, Harvard University, manuscript in preparation, 1995). Each grid cell is labeled with the country (or water area) occupying the major fraction of the area of the cell. The urban population of each country was assigned to specific locations using the longitude/latitude of large cities from Rand McNally (1987), scaling the city populations by the ratio of the urban population to the Rand urban population for each country. The remaining population was distributed over the habitable areas of each country, using a digital data base developed at the NASA Goddard Institute for Space Studies (Lerner, et al., 1988) for the purpose of locating animals. These population density maps were used as surrogates to allocate the default inventory to the $1^\circ \times 1^\circ$ grid and to aggregate the gridded emissions to the per country basis needed for this work. The regional inventories that were received in gridded format may have used additional surrogates to allocate the emissions to the 1° resolution grid; therefore, a small uncertainty is introduced in the per country emissions obtained from aggregating the final gridded inventory using the Logan country code identifiers. This uncertainty is smaller than the uncertainties associated with the emissions estimation.

Table A.2.1 presents the per country estimates of anthropogenic sulfur emissions in 1985 aggregated from the GEIA Version 1A inventory. Global

emissions total is 65.1 Tg S y^{-1} . Emissions are strongly localized in the highly populated and industrialized regions in Eastern North America, and across Europe from the United Kingdom over Central Europe to the Donbas region in Russia. Outside these areas are smaller regions or hot spots with quite large emissions, either in connection with densely populated areas with developed industries, or in connection with exploitation of fuels or mineral reserves. Figure 2 summarizes the latitudinal distribution of the emissions; the increase in emissions at latitude $\sim 68^\circ\text{N}$ is due to non-ferrous metal smelter operations in the Kola Peninsula.

A.3. GLOBAL ANTHROPOGENIC SULFUR EMISSIONS IN 1990

A.3.1 Methodology and Data Sources

A global inventory of anthropogenic sulfur emissions for 1990 is being developed as a collaborative effort between RIVM, Bilthoven, The Netherlands, IMW-TNO, Delft, The Netherlands and Brookhaven National Laboratory, Upton, NY, USA. The Dutch effort is part of the Emission Database for Global Atmospheric Research (EDGAR) project (Baars, et al., 1991, Berdowski, 1992, Olivier, et al., 1994). This section describes the methodologies and data sources used to compile an initial version of the inventory. Additional work is in progress to refine these estimates using more accurate regional inventories.

Anthropogenic sulfur sources were divided into four main source categories: fossil fuel combustion (including peat), biofuel combustion, industrial processes, and land use. Calculations were performed on a per country basis and aggregated to 13 major world regions/countries, as shown in Table A.3.1.1a. Fossil fuel and biofuel combustion calculations were done on a per sector basis, in which the following sectors were distinguished:

industry, commercial, residential, other sector, power generation, other fuel transformation sector (predominantly coke production and refineries), transportation (excluding marine bunkers), and international shipping. The definition of these sector largely follow the sectoral definitions used by the IEA and are summarized in Table A.3.1.1b. Industrial processes consist of metal production (copper, zinc, lead, iron, steel) and the production of sulfuric acid (H_2SO_4). Land use emissions relate to large scale biomass burning (deforestation and savannah burning) as well as local fires (agricultural waste burning).

To illustrate the general methodology and data sources used to develop the emissions estimates, a detailed description of the methodology used to estimate the emissions from the smelting of non-ferrous metals follows.

A.3.1.1. Smelting of Non-Ferrous Metals

Smelting of copper (Cu), lead (Pb), and zinc (Zn) are the main metallurgy industries contributing to sulfur emissions, with Cu the largest contributor. Some of the sulfur in the emissions from these industries is recovered; what is not recovered is released to the atmosphere. The following paragraphs describe how sulfur emissions from primary and secondary copper, lead and zinc smelters were estimated.

The production of copper, lead and zinc for each country was obtained from UN statistics (United Nations, 1992). Emission factors for these processes were computed assuming a simple stoichiometric relationship to give the release of sulfur dioxide (SO_2) in $t(S)/t(metal)$ (Kato and Akimoto, 1992); AP-42 (U.S. Environmental Protection Agency, 1985) and the work of Spiro et al. (1992) were also used as sources for the emission factors. For each

country the gross emissions for each metal were calculated by the sum of the product of the UN production figures and the appropriate primary and secondary emission factor.

The Minerals Yearbook published by the US Bureau of Mines (U.S. Department of the Interior, 1992) presents information on the countries which recover sulfur from industrial activities. For the majority of countries listed the yearbook presents reported values for the sulfur recovered from primary metal production; for some countries the recovery values are estimated. For some countries the sulfur recovered was tabulated according to the industrial processes (metallurgy, oil and gas, etc) from which it was recovered; thus recovery from metallurgy was explicitly given. For other countries the values presented were for total sulfur recovered from all sources.

For countries where the sulfur recovered from metallurgy was included in the Minerals Yearbook (U.S. Department of the Interior, 1992) this recovery was allocated to copper, lead and zinc smelting proportional to the gross emissions from primary production of each metal. The countries where the sulfur recovery was not allocated to the various industrial processes included China, North Korea, New Zealand, Pakistan, Taiwan, Zimbabwe, Qatar, and Turkey. With the exception of China, North Korea, and Turkey, metal smelting is not included in a country's industrial processes. For Turkey, the Minerals Yearbook specifies the sulfur recovered from petroleum sources; the recovery labeled 'other sources' was assumed to be from metallurgy.

The sulfur recovery per unit of total oil refining and gas production in Asia and the Pacific regions was computed. In these regions, only Australia, Japan, and India have metal smelters; the regional average recovery rate

(ton/PJ) was calculated using the values for these three countries. The sulfur recovered from the oil and gas industries in China and North Korea was estimated using the average recovery rate and each country's refinery throughput figures. Subtracting this value from the total sulfur recovered yields the recovery from metallurgy.

For each country, the sulfur recovered from metal production is subtracted from the gross emissions for this category to obtain the net emissions.

For some countries the net sulfur emissions calculated were negative. For countries which had explicit data for sulfur recovery from metallurgy in the Minerals Yearbook (U.S. Department of the Interior, 1992), reasons for the negative values might be: a) an incomplete time series of estimated metal production values might result in an underestimation of the metal production and thus of gross emissions; b) the sulfur content of ores used in the individual countries may have been higher than the stoichiometric ratio on which the emission factors were calculated, thus underestimating gross emissions; c) the sulfur recovery from 'Metallurgy' might have been related to a group of activities larger than primary metal production (i.e., it may also include recovery from secondary production of these metals); and d) an error may have occurred in either metal production and/or sulfur recovery data. Negative emissions were obtained in India, Mexico, North Korea, the Netherlands, and the Philippines. Regional NET emission factors were computed based on the net emissions and production figures for all other countries; the appropriate regional factor was applied to estimate the net emissions directly in those countries where emissions estimates had resulted in negative values.

For countries which did not have explicit data for sulfur recovery from

metallurgy in the Minerals Yearbook (U.S. Department of the Interior, 1992) the negative values could be due to: a) derived estimates for sulfur recovery from oil and gas and/or for recovery from metallurgy that were very different from the values used; or b) same reasons presented in the preceding paragraph. For these countries, regional recovery rates per unit refining/production were calculated for sulfur recovery from oil refining and gas and then applied to the oil and gas production data to yield the oil and gas recovery. Subtracting this number from the total sulfur recovery yielded metallurgy component. For a subset of these countries the sulfur recovered from oil and gas exceeded the total sulfur recovered. For these countries, a regional sulfur recovery rate for metallurgy was computed first. If this estimate was smaller than the total sulfur recovery for the country, the difference was taken to be the sulfur recovered from oil and gas industries. If the estimate was larger than the total sulfur recovery, all the recovery was assumed to be from metallurgy and net emissions were adjusted accordingly.

Some of the sulfur recovered is used for the production of sulfuric acid (H_2SO_4); a small fraction of this sulfur is not converted into H_2SO_4 but is emitted into the atmosphere. Kato and Akimoto (1992) estimate that between 2 and 5% of the sulfur input is emitted to the atmosphere; this amount depends upon the efficiency of the conversion to SO_3 . AP-42 (U.S. Environmental Protection Agency, 1985) presents a linear relationship to determine the emission factor of the SO_2 from sulfuric acid plants as a function of the above conversion. Kato and Akimoto (1992) quote 98% conversion efficiency for Japan, 97% for South Korea and 95.5% for the other Asian countries; these figures take into account the difference in the efficiency of plants and the fuel gas emission control. A similar high conversion efficiency of 98% can

also be assumed for most of the countries in western Europe, for the US and for Canada. The sulfuric acid production was obtained from the UN statistics (United Nations, 1992) and the emissions from sulfuric acid production were calculated. These values were added to the net emissions from metallurgy to give total sulfur emissions from this sector.

A.3.2 Emissions in the United States, Canada and Western European countries.

The methodologies used to develop these initial estimates do not account completely for the high levels of emissions control that are in effect in the industrialized areas of the world. Therefore, data from the following inventories should be considered more appropriate for the geographic areas covered: for the United States the U.S. Environmental Protection Agency (EPA) 1990 Interim Inventory (1993); for Canada the inventory compiled by the Pollution Data Analysis Division of Environment Canada (M. Deslauries, personal communication, 1995); for European countries the CORINAIR 90 inventory (G. McInnes, European Environment Agency, personal communication, 1995); and the inventory prepared for the Long Term Ozone Simulation Model (LOTOS) (Berdowski and Zandveld, 1995). The European inventories do not include the same countries; in the areas where they overlap the different estimates are currently being studied.

A.3.3. Initial Results

An overall summary of the 1990 global SO₂ emissions from anthropogenic activities by main source category and sector is presented in Table A.3.3.1a. Table A.3.3.1b presents emissions on a by-country basis. This table also includes emission estimates from the regional inventories described in Section

3.3.2. In estimating the emissions from European countries the EDGAR and LOTOS systems addressed the pre-1990 countries, (for example, Czechoslovakia), while the CORINAIR90 addressed the post-1990 countries (Czech Republic and Slovakia). Global total emissions are estimated at 75 TgS/year using the EDGAR values and at 71 TgS/year using estimates from regional inventories.

The following studies were developed using the EDGAR estimates because the sectoral resolutions needed were not always available from the regional inventories. The principal characteristics of SO₂ emissions from anthropogenic sources are presented in Table A.3.3.2, where emissions are reported for each main region and for each main source category. Fossil fuel combustion is the main contributing source category, at almost 80% of the anthropogenic global total, with more than half of these emissions originating in the USA, OECD Europe, the former USSR, and China regions. Industrial processes are the second largest contributing source category with 15% of global total, followed by land use at 5% and biofuels use at 1%. In the Latin America and Africa regions emissions from fossil fuel use account for less than 50% of the regional total due to the high contribution of land use and industrial emissions. Emissions from industrial processes are also important in the Oceania region; emissions from land use also have a relatively high contribution to regional emissions in the India region.

Table A.3.3.3 SO₂ presents emissions from the fossil fuel use source category by sector and region. The power generation sector is the largest contributor to emissions from this source category at 48% of the total followed by the industrial sector at 25%. This is the result of the high consumption of coal in these sectors, making coal combustion the highest contributor to emissions from fossil fuel use source category. The aggregate

statistics for the 'Commercial', 'Residential' and 'Other' sectors are often not well separated; this could result in the relatively low contribution from these three sectors to the emissions from the fossil fuel use source category.

About 70% of global emissions from the fossil fuel use source category originate in four regions: USA, OECD Europe, former USSR and China. The China region contributes about 30% of the global emissions from industrial use of fossil fuels and over 50% to the global emissions from residential use of fossil fuel. Due to the high consumption of coal and/or the high effective emission factors for coal combustion, the power generation sector contributes 60 to 70% of the total regional emissions for this source category in the Canada, USA, Eastern Europe, and Oceania regions. Coal consumption in the industrial and residential sectors in the China region is relatively high; these sectors contribute about 40% and 15% respectively of the regional emissions from the fossil fuel use source category. For the India and Japan regions the transportation sector has a relatively high contribution of about 15% to the regional emissions from the fossil fuel use source category, which is probably the result of high coal consumption in rail transport. The use of heavy fuel oils with high sulfur content as marine bunker fuels predominates over other fuels; combustion of these fuels accounts for about 5% of the global emissions from the fuel use source category. In the Middle East and East Asia regions marine bunkers contribute a relatively high 15% to the regional emissions from fossil fuel use, the result of a very high consumption of bunker fuel in the United Arab Emirates and Singapore.

Biofuel combustion is only a minor source compared to the other three main source categories. Table A.3.3.4 presents the distribution of emissions from this category by sector and by region. The total global energy output

from biofuels has been estimated at 49.5 EJ (Hall et al., 1994); about 78% is assumed to be used in the residential sector where fuel wood is the dominant type. The remaining 22% is related to industrial consumption, mostly in the form of wastes. We can clearly distinguish two groups of regions in the industrial and residential sectors using biofuels, developed regions and less developed regions. Developed regions contribute at least 80% to regional biofuel emissions. About 50% of the global emissions from biofuels originates from industry in the OECD Europe and USA regions (each about 25%), while residential emissions in the India and China regions together contribute another quarter (17% and 10%, respectively). The 58% relative contribution of the industrial sector to emissions from biofuel use is much higher than the fraction of biofuel consumption in this sector; the high contribution is the result of the higher emission factors for non-woody biofuels. For example, black liquor used in the Canada, OECD Europe and Oceania regions has a very high emission factor of 1000 g/GJ as compared with 5 g/GJ for fuel wood.

Table A.3.3.5. presents emissions from the industrial processes source category by sector and region. More than 50% of emissions from this source category stem from primary and secondary copper production; the production of zinc contributes another 20% and the production of H_2SO_4 contributes another 15% to these emissions. Copper production in the Latin America, OECD Europe and the former USSR regions contribute about 30% of the emissions from the industrial processes source category. Production of H_2SO_4 accounts for approximately 50% of the regional emissions in the India region. Iron and steel, although regionally important as in the case of Japan, are minor sources of emissions from the industrial processes source category. Except for zinc production in the OECD Europe region, copper production in the USA

and China regions, and zinc and H_2SO_4 production in the former USSR region, which contribute about 5% each to the emissions from the industrial processes source category, the remaining emissions from this category are scattered over various sectors and regions.

Emissions from the land use sector, presented in Table A.3.3.6, stem from large scale biomass burning and agricultural waste burning with a global ratio of 2/3 and 1/3. Biomass burning occurs predominantly in the Africa and Latin America regions, where deforestation and savannah burning together contribute about 40% and 20%, respectively, to global emissions from the land use sector. Approximately 35% of emissions from agricultural waste burning originate in the India and China regions.

In general the distribution of global SO_2 emissions is largely dependent on the local economic structure and availability of resources, whether it is the use of coal, the production of metals, or regional agricultural practices. Although in a number of regions emission reduction technologies are being applied to some extent in the use of coal for power generation, in the iron and steel industry, and in copper production, these sectors contribute about 66.7% of global SO_2 emissions from anthropogenic sources.

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Table A.2.1 SO₂ Emissions from Anthropogenic Activities in 1985

Country	Emissions (metric tons S)	Country	Emissions (metric tons S)
AFGHANISTAN	4,240	EGYPT	279,500
ALBANIA	28,407	EL SALVADOR	7,214
ALGERIA	130,775	EQ GUINEA	40
ANGOLA	2,992	ETHIOPIA	6,928
ANTIGUA	211	FALKLAND	37
ARGENTINA	208,977	FAROE I.	590
AUSTRALIA	805,465	FIJI	500
AUSTRIA	116,250	FINLAND	261,845
BAHAMAS	14,705	FRANCE	625,466
BAHRAIN	71,000	FRGUIANA	472
BANGLADESH	26,696	FRPOLYNE	574
BARBADOS	3,376	GABON	3,619
BELGIUM	196,616	GAMBIA	95
BELIZE	125	GHANA	11,581
BENIN	561	GREECE	268,163
BERMUDA	744	GREENLAND	87
BHUTAN	236	GRENADA	5
BOLIVIA	8,304	GUADELPE	1,185
BOTSWANA	11,016	GUATEMALA	11,595
BRAZIL	1,187,697	GUINEA	3,341
BRUNEI	700	GUINEA-B	296
BULGARI	316,960	GUYANA	4,588
BURKINA	829	HAITI	1,529
BURMA	17,300	HONDURAS	3,801
BURUNDI	368	HONG KONG	72,000
CAFRREP	263	HUNGARY	670,067
CAMEROON	6,651	ICELAND	2,028
CANADA	1,799,512	INDIA	1,411,267
CAPE VERDE	152	INDONESI	217,950
CHAD	260	IRAN	572,680
CHILE	1,088,383	IRAQ	159,996
CHINA	9,037,328	IRELAND	61,046
COLOMBIA	65,798	ISRAEL	141,518
COMOROS	40	ITALY	1,038,335
CONGO	7,677	IVORY COAST	12,727
COOK ISLAND	2	JAMAICA	28,075
COSTA RICA	4,098	JAPAN	438,262
CUBA	119,066	JORDAN	21,222
CYPRUS	12,174	KAMPUCHEA	1,358
CZECHSLOVAKIA	1,017,013	KENYA	20,486
DENMARK	154,430	KIRIBATI	2
DJIBOUTI	5,786	KUWAIT	196,875
DOMINICA	22	LAOS	3,384
DOMREP	28,072	LEBANON	22,145
ECUADOR	41,510	LESOTHO	38
EGERMAN	2,210,679	LIBERIA	2,738

Table A.2.1 SO₂ Emissions from Anthropogenic Activities in 1985

Country	Emissions (metric tons S)	Country	Emissions (metric tons S)
LIBYA	71,804	SEYCHELLES	378
LIECHTENSTEIN	3,162	SIERRA LEONE	3,400
LUXEMBURG	6,284	SINGAPORE	82,375
MADAGASCAR	3,415	SOLOMONI	26
MALAWI	1,664	SOMALIA	2,994
MALAYSIA	125,694	SOUTH AFRICA	930,659
MALDIVES	8	SOUTH KOREA	444,410
MALI	478	SPAIN	1,141,738
MALTA	7,270	SRI LANKA	11,805
MARTINIQUE	3,868	ST LUCIA	28
MAURITANIA	694	STCHRS-N	5
MAURITIUS	2,108	STVINC&G	4
MEXICO	1,314,600	SUDAN	8,476
MONGOLIA	41,296	SURINAM	3,631
MOROCCO	80,430	SWAZILAN	4,037
MOZAMBIQUE	3,860	SWEDEN	137,043
N. CALEDONIA	7,004	SWITZERLAND	16,338
NAMIBIA	51,650	SYRIA	226,163
NANTILLE	38,030	TAIWAN	340,083
NAURU	579	TANZANIA	7,592
NEPAL	4,830	THAILAND	252,103
NETHERLANDS	151,190	TOGO	800
NEW ZEALAND	55,819	TONGA	4
NICARAGUA	5,881	TRINIDAD & TOBAGO	20,295
NIGER	1,806	TUNISIA	50,866
NIGERIA	26,082	TURKEY	479,122
NORTH KOREA	263,564	TURKS&C.	0
NORWAY	51,279	TUVALU	0
OMAN	8,050	U.K.	1,878,465
PAKISTAN	180,116	U.S.A.	10,784,072
PALESTIN	11,315	UARABEMI	37,389
PANAMA	23,953	UGANDA	1,456
PAPUANG	5,110	URUGUAY	11,597
PARAGUAY	3,145	USSR/TOTAL	12,264,932
PERU	493,723	VANUATU	456
PHILIPPINES	247,952	VENEZUELA	459,956
POLAND	2,086,481	VIETNAM	21,900
PORTUGA	96,354	W. SAHARA	245
QATAR	7,365	W. SAMOA	42
REUNION	171	WGERMAN	1,114,631
ROMANIA	767,629	YEMEN/NORTH	1,447
RWANDA	972	YEMEN/SOUTH	33,365
SAN MARTIN	1,719	YUGOSLAVIA	759,165
SAOTOME&	3	ZAIRE	1,027,972
SAUDI ARABIA	499,174	ZAMBIA	147,914
SENEGAL	7,174	ZIMBABWE	99,462

Table A.2.1 SO₂ Emissions from Anthropogenic Activities in 1985

Country	Emissions (metric tons S)	Country	Emissions (metric tons S)
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Total 65,056,490

Table A.3.1.1a. Definition of World Regions in EDGAR¹ Project.

EDGAR Region	Description/list of countries
A: CANADA	Canada
B: USA	USA
C: LATIN AMERICA	Central and South America
D: AFRICA	Africa
E: OECD EUROPE	European Union (15), Iceland, Norway, Switzerland, excluding Turkey (allocated in 'Middle East')
F: EASTERN EUROPE	Former Centrally Planned Europe: Albania, Bulgaria, former Czechoslovakia, Hungary, Poland, Romania, former Yugoslavia
G: CIS (FORMER USSR)	Former USSR
H: MIDDLE EAST	Afghanistan, Bahrain, Cyprus, Iran, Iraq, Israel, Jordan, Kuwait, Lebanon, Oman, Qatar, Saudi Arabia, Syria, Turkey, United Arab Emirates, Yemen (united)
I: INDIA REGION	Bangladesh, Bhutan, India, Maldives, Myanmar (former Burma), Nepal, Pakistan, Sri Lanka
J: CHINA REGION	China, Hong Kong, Kampuchea (former Cambodia), North Korea (Dem. People's Rep.), Laos, Macau, Mongolia, Vietnam
K: EAST ASIA	Brunei, Indonesia, South Korea (Rep. of), Malaysia, Papua New Guinea, Philippines, Thailand, East Timor
L: OCEANIA	Australia, New Zealand, minor Pacific islands
M: JAPAN	Japan

¹ Emission Database for Global Atmospheric Research (EDGAR) (Baars et al., 1991; Berdowski, 1992; Oliver et al., 1994).

Table A.3.1.1b. Definition of Sectors Used in EDGAR for Fuel and Biofuels Combustion Source Categories

EDGAR	IEA ¹	Remarks
Industry	Industry	Excluding the energy sector (e.g. power generation, refineries)
Commercial	Commercial	Commercial and public services
Residential	Residential	Household dwellings
Other	Other end-use sectors	IEA sub-sectors 'Agriculture' and 'Other-Non-Specified'
Transport	Transport	Road, rail, air, and water transport, excluding marine bunkers
International ships	Marine bunkers	
Power plants	Electricity	Public electricity, autoproducers of generation electricity, CHP plants
Other transf.	Other fuel	Refineries, coke ovens, blast furnaces, transformation gas works, district heating, etc.

¹ International Energy Agency.

Table A.3.3.1a. Summary of Anthropogenic SO₂ Emissions in 1990

Sector	Emissions (metric tons S)	Subtotals
Power generation	28,440,000	
Fossil fuel combustion		
Commercial	1,426,000	
Residential	3,334,000	
Others	1,843,000	
Other transformation (coke & refineries)	5,421,000	
Traffic		
International shipping	2,465,000	
All transport excl. international shipping	1,402,000	
Industry		
Combustion of fossil fuels	15,080,000	59,411,000
Production processes		
Copper smelters	6,689,000	
Lead smelters	388,300	
Zinc smelters	2,165,000	
Iron & steel industry	434,200	
Misc industrial processes (H ₂ SO ₄ , etc.)	1,750,000	11,426,500
Biofuel combustion		
Industrial	476,800	
Residential	339,700	
Other	1,323	817,823
Deforestation & savannah burning	2,596,000	
Agricultural waste burning	1,263,000	3,859,000
Grand total	75,514,323	

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Code	Country	EDGAR	LOTOS	Regional	Best Estimate
AFG	afghanistan	36,897			36,897
ALB	albania	36,523	55,900		55,900
DZA	algeria	93,430			93,430
ASM	american samoa	456			456
AGO	angola	147,610			147,610
AIA	anguilla	1			1
ATG	antigua and barbuda	1,073			1,073
ARG	argentina	173,568			173,568
ABW	aruba	4			4
AUS	australia	689,131			689,131
AUT	austria	112,836	86,219	46,500	46,500
BHS	bahamas	4,823			4,823
BHR	bahrain	19,134			19,134
BGD	bangladesh	52,454			52,454
BRB	barbados	3,215			3,215
BEL	belgium	1,116,896	181,281	153,500	153,500
BLZ	belize	2,513			2,513
BEN	benin	13,733			13,733
BMU	bermuda	2,138			2,138
BTN	bhutan	962			962
BOL	bolivia	52,455			52,455
BWA	botswana	77,881			77,881
BRA	brazil	1,135,448			1,135,448
VGB	british virgin islands	267			267
BRN	brunei	1,117			1,117
BGR	bulgaria	926,645	751,192	1,004,000	1,004,000
BFA	burkina faso	23,541			23,541
BDI	burundi	11,708			11,708
CMR	cameroon	38,948			38,948
CAN	canada	1,470,391		1,470,371	1,470,371
CPV	cape verde	271			271
CYM	cayman islands	803			803
CAF	central african republic	84,589			84,589
TCD	chad	49,295			49,295
CHL	chile	1,134,492			1,134,492
CHN	china	11,543,018			11,543,018

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Code	Country	EDGAR	LOTOS	Regional	Best Estimate
COL	colombia	123,505			123,505
COM	comoros	527			527
COG	congo	15,267			15,267
COK	cook islands	1			1
CRI	costa rica	16,425			16,425
CIV	cote d'ivoire (ivory coast)	73,565			73,565
	croatia			90,000	90,000
CUB	cuba	157,859			157,859
CYP	cyprus	17,841			17,841
	czech republic			931,500	931,500
CSK	czechoslovakia	1,080,981	1,048,602		1,048,602
DNK	denmark	130,362	106,739	99,000	99,000
DJI	djibouti	3,512			3,512
DMA	dominica	272			272
DOM	dominican republic	21,744			21,744
ECU	ecuador	49,716			49,716
EGY	egypt	323,632			323,632
SLV	el salvador	10,955			10,955
GNQ	equatorial guinea	1,279			1,279
	estonia			137,500	137,500
ETH	ethiopia	89,427			89,427
FJI	fiji	2,555			2,555
FIN	finland	272,689	106,986	113,500	113,500
FRA	france	978,970	562,705	650,000	650,000
GUF	french guiana	2,812			2,812
PYF	french polynesia	2,047			2,047
GAB	gabon	11,164			11,164
GMB	gambia	907			907
DEU	german fed republic	930,459		456,000	456,000
DDR	german democratic repub	2,596,854	2,173,848	2,172,500	2,172,500
GHA	ghana	38,347			38,347
GIB	gibraltar	10,286			10,286
GRC	greece	409,316	290,672	320,500	320,500
GRD	grenada	539			539
GLP	guadeloupe	3,788			3,788
GUM	guam	4,759			4,759

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Code	Country	EDGAR	LOTOS	Regional	Best Estimate
GTM	guatemala	17,456			17,456
GIN	guinea	19,229			19,229
GNB	guinea-bissau	3,044			3,044
GUY	guyana	6,596			6,596
HTI	haiti	3,588			3,588
HND	honduras	12,918			12,918
HKG	hong kong	121,093			121,093
HUN	hungary	328,406	318,173	452,500	452,500
ISL	iceland	2,029			2,029
IND	india	2,155,707			2,155,707
IDN	indonesia	338,508			338,508
IRN	iran, islamic republic of	574,951			574,951
IRQ	iraq	146,915			146,915
NTZ	iraq-saudi arabia n. zone	6,579			6,579
IRL	ireland	105,562	96,366	89,000	89,000
ISR	israel	143,153			143,153
ITA	italy	1,353,753	1,136,396	1,126,500	1,126,500
JAM	jamaica	170,603			170,603
JPN	japan	1,549,205			1,549,205
JOR	jordan	37,383			37,383
KHM	kampuchea (cambodia)	12,682			12,682
KEN	kenya	53,705			53,705
KIR	kiribati	4			4
PRK	korea, north	708,562			708,562
KOR	korea, south	1,158,910			1,158,910
KWT	kuwait	92,083			92,083
LAO	lao peoples dem repub	13,883			13,883
	latvia			57,500	57,500
LBN	lebanon	25,935			25,935
LSO	lesotho	350			350
LBR	liberia	20,316			20,316
LBY	libyan arab jamahiriya	76,563			76,563
	lithuania			111,000	111,000
LUX	luxembourg	14,178	11,262	7,000	7,000

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Code	Country	EDGAR	LOTOS	Regional	Best Estimate
MAC	macau	3,681			3,681
MDG	madagascar	25,618			25,618
MWI	malawi	4,468			4,468
MYS	malaysia	161,620			161,620
MDV	maldives	242			242
MLI	mali	44,547			44,547
MLT	malta	10,651		3,000	3,000
MTQ	martinique	4,826			4,826
MRT	mauretania	29,203			29,203
MUS	mauritius	3,866			3,866
MEX	mexico	1,064,054			1,064,054
MNG	mongolia	28,307			28,307
MSR	montserrat	1			1
MAR	morocco	108,753			108,753
MOZ	mozambique	74,447			74,447
MMR	myanmar (former burma)	51,417			51,417
NAM	namibia	70,344			70,344
NRU	nauru	453			453
NPL	nepal	8,229			8,229
NLD	netherlands	101,440	101,440	100,500	101,440
ANT	netherlands antilles	69,800			69,800
NCL	new caledonia	4,989			4,989
NZL	new zealand	48,313			48,313
NIC	nicaragua	14,038			14,038
NER	niger	31,684			31,684
NGA	nigeria	153,125			153,125
NOR	norway	78,992	26,598	27,000	27,000
OMN	oman	17,271			17,271
PAK	pakistan	155,958			155,958
PAN	panama	35,074			35,074
PNG	papua new guinea	16,273			16,273
PRY	paraguay	20,451			20,451
PER	peru	285,810			285,810
PHL	philippines	300,004			300,004
POL	poland	1,940,145	1,389,848	1,636,500	1,636,500
PRT	portugal	173,470	133,428	141,500	141,500

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Code	Country	EDGAR	LOTOS	Regional	Best Estimate
PRI	puerto rico	360			360
QAT	qatar	5,093			5,093
REU	reunion	3,653			3,653
ROM	romania	736,982	698,576	655,500	655,500
RWA	rwanda	9,475			9,475
STP	sao tome & principe	249			249
SAU	saudi arabia	403,441			403,441
SEN	senegal	30,245			30,245
SYC	seychelles	487			487
SLE	sierra leone	10,848			10,848
SGP	singapore	424,806			424,806
	slovakia			271,000	271,000
	slovenia			98,000	98,000
SLB	solomon islands	474			474
SOM	somalia	25,724			25,724
ZAF	south africa	977,303			977,303
ESP	spain	1,100,719	699,206	1,103,000	1,103,000
LKA	sri lanka	20,749			20,749
SHN	st helena	1			1
	st kitts & nevis				
KNA	(st christop	270			270
LCA	st lucia	535			535
	st vincent & the				
VCT	grenadine	275			275
	st-pierre &				
SPM	miquelon	267			267
SDN	sudan	173,483			173,483
SUR	suriname	9,168			9,168
SWZ	swaziland	200			200
SWE	sweden	225,204	52,282	52,500	52,500
CHE	switzerland	38,987	33,019	22,000	22,000
	syrian arab				
SYR	republic	92,860			92,860
TWN	taiwan	476,621			476,621
	tanzania, united				
TZA	republic	107,246			107,246
THA	thailand	360,934			360,934
	timor timur (east				
TMP	timor)	49			49

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Code	Country	EDGAR	LOTOS	Regional	Best Estimate
TGO	togo	9,843			9,843
TON	tonga	232			232
TTO	trinidad and tobago	7,417			7,417
TUN	tunesia	101,386			101,386
TUR	turkey	761,005			761,005
TCA	turks & caicos islands	1			1
TUV	tuvalu	1			1
UGA	uganda	35,838			35,838
ARE	united arab emirates	214,362			214,362
GBR	united kingdom	2,178,525	1,862,154	1,893,500	1,893,500
USA	united states (usa)	12,465,230		10,969,496	10,969,496
URY	uruguay	19,298			19,298
SUN	ussr (former)	11,394,139	12,608,429		12,608,429
VUT	vanuatu	10			10
VEN	venezuela	193,035			193,035
VNM	vietnam	85,375			85,375
VIR	virgin islands (us)	88,758			88,758
WLF	wallis & futuna	1			1
ESH	western sahara	756			756
WSM	western samoa	463			463
YEM	yemen	26,499			26,499
YUG	yugoslavia (former)	540,142	468,754		468,754
ZAR	zaire	367,990			367,990
ZMB	zambia	560,604			560,604
ZWE	zimbabwe	75,498			75,498
	Totals	75,219,157			71,317,702*

* This value is not the sum of all values in the column because some of the old political divisions (such as Czechoslovakia) and the corresponding new countries (Czech Republic and Slovakia) are all listed.

EDGAR is the Emissions Database for Global Atmospheric Research project (Baars et al., 1991; Berdowski, 1992; Olivier et al., 1994).

LOTOS is the inventory compiled for the Long Term Ozone Simulation Model (Berdowski and Zandveld, 1995).

Table A.3.3.1b. SO₂ Emissions from Anthropogenic Activities in 1990 (metric ton S)

Values in the Best column:

For Canada, total from the inventory compiled by the Pollution Data Analysis Division of Environment Canada (M. Deslauriers, Pollution Data Analysis Division, Environment Canada, personal communication, 1995).

For European countries, totals from the CORINAIR90 inventory (G. McInnes, European Environment Agency, personal communication, 1995).

For US, total from the US Environmental Protection Agency (EPA) 1990 Interim Inventory (1993).

For other countries, the EDGAR estimates.

Table A.3.3.2 SO₂ emissions from activities in 1990 (metric tons S)

Unit: Pg S/yr	Industrial				
EDGAR Region	Fossil fuel	Biofuel	Processes	Land Use	Total
ED.A: CANADA	1.030	0.192	1.004	0.026	1.352
ED.B: USA	11.332	0.023	1.719	0.105	12.465
ED.C: LATIN AMERICA	2.300	0.017	0.756	0.884	4.920
ED.D: AFRICA	1.768	0.067	2.236	1.742	4.334
ED.E: OECD EUROPE	9.764	0.219	0.749	0.105	12.324
ED.F: EASTERN EUROPE	4.814	0.001	2.432	0.025	5.590
ED.G: CIS (FORMER USSR)	8.839	0.003	0.104	0.121	11.395
ED.H: MIDDLE EAST	2.409	0.014	0.111	0.095	2.621
ED.I: INDIA REGION	1.883	0.091	1.234	0.359	2.446
ED.J: CHINA REGION	11.415	0.140	0.523	0.205	12.994
ED.K: EAST ASIA	2.040	0.026	0.244	0.173	2.762
ED.L: OCEANIA	0.474	0.024	0.209	0.012	0.754
ED.M: JAPAN	1.334	0.000	11.426	0.006	1.549
TOTAL	59.403	0.818		3.859	75.505

Unit: Percentage of regional total	Industrial				
EDGAR Region	Fossil fuel	Biofuel	Processes	Landuse	Total
ED.A: CANADA	76.2	14.2	7.7	1.9	100.0
ED.B: USA	90.9	0.2	8.1	0.8	100.0
ED.C: LATIN AMERICA	46.7	0.4	34.9	18.0	100.0
ED.D: AFRICA	40.8	1.6	17.4	40.2	100.0
ED.E: OECD EUROPE	79.2	1.8	18.1	0.8	100.0
ED.F: EASTERN EUROPE	86.1	0.0	13.4	0.5	100.0
ED.G: CIS (FORMER USSR)	77.6	0.0	21.3	1.1	100.0
ED.H: MIDDLE EAST	91.9	0.5	3.9	3.6	100.0
ED.I: INDIA REGION	77.0	3.7	4.6	14.7	100.0
ED.J: CHINA REGION	87.9	1.1	9.5	1.6	100.0
ED.K: EAST ASIA	73.8	1.0	18.9	6.3	100.0

Table A.3.3.2 SO₂ emissions from activities in 1990 (metric tons S)

ED.L: OCEANIA	62.9	3.2	32.4	1.6	100.0
ED.M: JAPAN	86.1	0.0	13.5	0.4	100.0
TOTAL	78.7	1.1	15.1	5.1	100.0

Unit: Percentage of source total		Industrial			Total
EDGAR Region	Fossil fuel	Biofuel	Processes	Landuse	
ED.A: CANADA	1.7	23.4	0.9	0.7	1.8
ED.B: USA	19.1	2.8	8.8	2.7	16.5
ED.C: LATIN AMERICA	3.9	2.1	15.0	22.9	6.5
ED.D: AFRICA	3.0	8.2	6.6	45.1	5.7
ED.E: OECD EUROPE	16.4	26.8	19.6	2.7	16.3
ED.F: EASTERN EUROPE	8.1	0.2	6.6	0.7	7.4
ED.G: CIS (FORMER USSR)	14.9	0.3	21.3	3.1	15.1
ED.H: MIDDLE EAST	4.1	1.7	0.9	2.5	3.5
ED.I: INDIA REGION	3.2	11.2	1.0	9.3	3.2
ED.J: CHINA REGION	19.2	17.1	10.8	5.3	17.2
ED.K: EAST ASIA	3.4	3.2	4.6	4.5	3.7
ED.L: OCEANIA	0.8	2.9	2.1	0.3	1.0
ED.M: JAPAN	2.2	0.0	1.8	0.2	2.1
TOTAL	100.0	100.0	100.0	100.0	100.0

Unit: Percentage of global total		Industrial			Total
EDGAR Region	Fossil fuel	Biofuel	Processes	Landuse	
ED.A: CANADA	1.4	0.3	0.1	0.0	1.8
ED.B: USA	15.0	0.0	1.3	0.1	16.5
ED.C: LATIN AMERICA	3.0	0.0	2.3	1.2	6.5
ED.D: AFRICA	2.3	0.1	1.0	2.3	5.7
ED.E: OECD EUROPE	12.9	0.3	3.0	0.1	16.3
ED.F: EASTERN EUROPE	6.4	0.0	1.0	0.0	7.4
ED.G: CIS (FORMER USSR)	11.7	0.0	3.2	0.2	15.1
ED.H: MIDDLE EAST	3.2	0.0	0.1	0.1	3.5

Table A.3.3.2 SO₂ emissions from activities in 1990 (metric tons S)

ED.I: INDIA REGION	2.5	0.1	0.1	0.5	3.2
ED.J: CHINA REGION	15.1	0.2	1.6	0.3	17.2
ED.K: EAST ASIA	2.7	0.0	0.7	0.2	3.7
ED.L: OCEANIA	0.6	0.0	0.3	0.0	1.0
ED.M: JAPAN	1.8	0.0	0.3	0.0	2.1
TOTAL	78.7	1.1	15.1	5.1	100.0

Table A.3.3.3. SO₂ Emissions from Fossil Fuel Use Source Category in 1990

Unit: Gg S/yr EDGAR Region	Industry	Comm	Resid	Other	Power Gen.	Other Transf.	Transp	Internat. Ships	Total
ED.A: CANADA	141	18	14	6	688	132	19	12	1,030
ED.B: USA	1,964	222	79	98	7,187	983	228	571	11,332
ED.C: LATIN AMERICA	668	13	21	133	756	526	49	133	2,300
ED.D: AFRICA	397	15	24	47	920	214	20	133	1,768
ED.E: OECD EUROPE	2,402	167	872	86	4,464	943	125	705	9,764
ED.F: EASTERN EUROPE	654	7	216	310	3,406	188	21	12	4,814
ED.G: CIS (FORMER USSR)	2,273	828	0	269	4,370	858	127	113	8,839
ED.H: MIDDLE EAST	423	0	122	286	710	520	26	323	2,409
ED.I: INDIA REGION	591	1	43	29	776	160	270	14	1,883
ED.J: CHINA REGION	4,629	136	1,742	488	3,622	434	296	68	11,415
ED.K: EAST ASIA	485	13	186	27	688	302	23	316	2,040
ED.L: OCEANIA	61	3	3	6	309	63	18	11	474
ED.M: JAPAN	388	4	12	59	540	98	180	54	1,334
TOTAL	15,076	1,426	3,334	1,843	28,436	5,421	1,402	2,465	59,403

Unit: Percentage of regional total EDGAR Region	Industry	Comm	Resid	Other	Power Gen.	Other Transf.	Transp	Internat. Ships	Total
ED.A: CANADA	13.7	1.7	1.4	0.6	66.8	12.8	1.9	1.2	100.0
ED.B: USA	17.3	2.0	0.7	0.9	63.4	8.7	2.0	5.0	100.0

Table A.3.3.3. SO₂ Emissions from Fossil Fuel Use Source Category in 1990

ED.C: LATIN AMERICA	29.1	0.6	0.9	5.8	32.9	22.9	2.2	5.8	100.0
ED.D: AFRICA	22.4	0.8	1.3	2.6	52.0	12.1	1.1	7.5	100.0
ED.E: OECD EUROPE	24.6	1.7	8.9	0.9	45.7	9.7	1.3	7.2	100.0
ED.F: EASTERN EUROPE	13.6	0.2	4.5	6.4	70.8	3.9	0.4	0.2	100.0
ED.G: CIS (FORMER USSR)	25.7	9.4	0.0	3.0	49.4	9.7	1.4	1.3	100.0
ED.H: MIDDLE EAST	17.5	0.0	5.1	11.9	29.5	21.6	1.1	13.4	100.0
ED.I: INDIA REGION	31.4	0.1	2.3	1.5	41.2	8.5	14.3	0.8	100.0
ED.J: CHINA REGION	40.5	1.2	15.3	4.3	31.7	3.8	2.6	0.6	100.0
ED.K: EAST ASIA	23.8	0.6	9.1	1.3	33.8	14.8	1.1	15.5	100.0
ED.L: OCEANIA	12.9	0.5	0.6	1.3	65.2	13.2	3.8	2.4	100.0
ED.M: JAPAN	29.1	0.3	0.9	4.4	40.5	7.3	13.5	4.0	100.0
TOTAL	25.4	2.4	5.6	3.1	47.9	9.1	2.4	4.2	100.0

Unit: Percentage of source total					Power	Other	Internat.		
EDGAR Region	Industry	Comm	Resid	Other	Gen.	Transf.	Transp	Ships	Total
ED.A: CANADA	1.0	1.0	0.0	0.0	2.0	2.0	1.0	0.0	2.0
ED.B: USA	13.0	15.6	2.4	5.3	25.3	18.1	16.3	23.2	19.1
ED.C: LATIN AMERICA	4.4	0.9	0.6	7.2	2.7	9.7	3.5	5.4	3.9
ED.D: AFRICA	2.6	1.0	0.7	2.5	3.2	3.9	1.4	5.4	3.0
ED.E: OECD EUROPE	15.9	11.7	26.2	4.6	15.7	17.4	8.9	28.6	16.4

Table A.3.3.3. SO₂ Emissions from Fossil Fuel Use Source Category in 1990

ED.F: EASTERN EUROPE	4.3	0.5	6.5	16.8	12.0	3.5	1.5	0.5	8.1
ED.G: CIS (FORMER USSR)	15.1	58.1	0.0	14.6	15.4	15.8	9.1	4.6	14.9
ED.H: MIDDLE EAST	2.8	0.0	3.7	15.5	2.5	9.6	1.8	13.1	4.1
ED.I: INDIA REGION	3.9	0.1	1.3	1.6	2.7	2.9	19.2	0.6	3.2
ED.J: CHINA REGION	30.7	9.5	52.3	26.5	12.7	8.0	21.1	2.8	19.2
ED.K: EAST ASIA	3.2	0.9	5.6	1.5	2.4	5.6	1.7	12.8	3.4
ED.L: OCEANIA	0.4	0.2	0.1	0.3	1.1	1.2	1.3	0.5	0.8
ED.M: JAPAN	2.6	0.3	0.4	3.2	1.9	1.8	12.8	2.2	2.2
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Unit: Percentage of global total					Power				Internat.
EDGAR Region	Industry	Comm	Resid	Other	Gen.	Other	Transp	Ships	Total
ED.A: CANADA	0.2	0.0	0.0	0.0	1.2	0.2	0.0	0.0	1.7
ED.B: USA	3.3	0.4	0.1	0.2	12.1	1.7	0.4	1.0	19.1
ED.C: LATIN AMERICA	1.1	0.0	0.0	0.2	1.3	0.9	0.1	0.2	3.9
ED.D: AFRICA	0.7	0.0	0.0	0.1	1.5	0.4	0.0	0.2	3.0
ED.E: OECD EUROPE	4.0	0.3	1.5	0.1	7.5	1.6	0.2	1.2	16.4
ED.F: EASTERN EUROPE	1.1	0.0	0.4	0.5	5.7	0.3	0.0	0.0	8.1
ED.G: CIS (FORMER USSR)	3.8	1.4	0.0	0.5	7.4	1.4	0.2	0.2	14.9
ED.H: MIDDLE EAST	0.7	0.0	0.2	0.5	1.2	0.9	0.0	0.5	4.1
ED.I: INDIA REGION	1.0	0.0	0.1	0.0	1.3	0.3	0.5	0.0	3.2

Table A.3.3.3. SO₂ Emissions from Fossil Fuel Use Source Category in 1990

ED.J: CHINA REGION	7.8	0.2	2.9	0.8	6.1	0.7	0.5	0.1	19.2
ED.K: EAST ASIA	0.8	0.0	0.3	0.0	1.2	0.5	0.0	0.5	3.4
ED.L: OCEANIA	0.1	0.0	0.0	0.0	0.5	0.1	0.0	0.0	0.8
ED.M: JAPAN	0.7	0.0	0.0	0.1	0.9	0.2	0.3	0.1	2.2
TOTAL	25.4	2.4	5.6	3.1	47.9	9.1	2.4	4.2	100.0

Table A.3.3.4. SO₂ Emissions from Biofuels Use Source Category in 1990

Unit: Gg S/yr			
EDGAR Region	Industrial	Residential	Total
ED.A: CANADA	191	0	192
ED.B: USA	19	4	23
ED.C: LATIN AMERICA	5	12	17
ED.D: AFRICA	3	64	67
ED.E: OECD EUROPE	218	1	219
ED.F: EASTERN EUROPE	1	0	1
ED.G: CIS (FORMER USSR)	2	0	3
ED.H: MIDDLE EAST	1	13	14
ED.I: INDIA REGION	9	83	91
ED.J: CHINA REGION	2	137	140
ED.K: EAST ASIA	4	23	26
ED.L: OCEANIA	22	2	24
ED.M: JAPAN	0	0	0
TOTAL	478	340	818

Unit: Percentage of regional total			
EDGAR Region	Industrial	Residential	Total
ED.A: CANADA	99.9	0.1	100.0
ED.B: USA	82.0	18.0	100.0
ED.C: LATIN AMERICA	28.7	71.3	100.0
ED.D: AFRICA	4.7	95.3	100.0
ED.E: OECD EUROPE	99.6	0.4	100.0
ED.F: EASTERN EUROPE	91.0	9.0	100.0
ED.G: CIS (FORMER USSR)	90.0	10.0	100.0
ED.H: MIDDLE EAST	5.5	94.5	100.0
ED.I: INDIA REGION	9.7	90.3	100.0
ED.J: CHINA REGION	1.8	98.2	100.0
ED.K: EAST ASIA	13.6	86.4	100.0

Table A.3.3.4. SO₂ Emissions from Biofuels Use Source Category in 1990

ED.L: OCEANIA	92.5	7.5	100.0
ED.M: JAPAN	87.4	12.6	100.0
TOTAL	58.5	41.5	100.0

Unit: Percentage of source total			
EDGAR Region	Industrial	Residential	Total
ED.A: CANADA	40.0	0.1	23.4
ED.B: USA	4.0	1.2	2.8
ED.C: LATIN AMERICA	1.0	3.6	2.1
ED.D: AFRICA	0.7	18.9	8.2
ED.E: OECD EUROPE	45.7	0.3	26.8
ED.F: EASTERN EUROPE	0.2	0.0	0.2
ED.G: CIS (FORMER USSR)	0.5	0.1	0.3
ED.H: MIDDLE EAST	0.2	3.8	1.7
ED.I: INDIA REGION	1.8	24.3	11.2
ED.J: CHINA REGION	0.5	40.4	17.1
ED.K: EAST ASIA	0.7	6.7	3.2
ED.L: OCEANIA	4.6	0.5	2.9
ED.M: JAPAN	0.0	0.0	0.0
TOTAL	100.0	100.0	100.0

Unit: Percentage of global total			
EDGAR Region	Industrial	Residential	Total
ED.A: CANADA	23.4	0.0	23.4
ED.B: USA	2.3	0.5	2.8
ED.C: LATIN AMERICA	0.6	1.5	2.1
ED.D: AFRICA	0.4	7.9	8.2
ED.E: OECD EUROPE	26.7	0.1	26.8
ED.F: EASTERN EUROPE	0.1	0.0	0.2
ED.G: CIS (FORMER USSR)	0.3	0.0	0.3

Table A.3.3.4. SO₂ Emissions from Biofuels Use Source Category in 1990

ED.H: MIDDLE EAST	0.1	1.6	1.7
ED.I: INDIA REGION	1.1	10.1	11.2
ED.J: CHINA REGION	0.3	16.8	17.1
ED.K: EAST ASIA	0.4	2.8	3.2
ED.L: OCEANIA	2.7	0.2	2.9
ED.M: JAPAN	0.0	0.0	0.0
TOTAL	58.5	41.5	100.0

Table A.3.3.5. SO₂ Emissions from the Industrial Processes Source Category in 1990

Unit: Gg S/yr EDGAR Region	Copper	Zinc	Lead	Iron & Steel	H ₂ SO ₄	TOTAL
ED.A: CANADA	47	24	7	1	25	104
ED.B: USA	618	61	41	10	274	1,004
ED.C: LATIN AMERICA	1,327	125	35	19	213	1,719
ED.D: AFRICA	627	32	16	0	81	756
ED.E: OECD EUROPE	1,099	710	110	86	231	2,236
ED.F: EASTERN EUROPE	460	127	25	30	107	749
ED.G: CIS (FORMER USSR)	1,336	448	76	107	465	2,432
ED.H: MIDDLE EAST	86	0	2	3	13	103
ED.I: INDIA REGION	20	25	2	7	57	111
ED.J: CHINA REGION	550	362	46	71	204	1,234
ED.K: EAST ASIA	327	141	10	21	23	523
ED.L: OCEANIA	128	86	15	5	10	244
ED.M: JAPAN	65	23	2	72	47	209
TOTAL	6,689	2,165	388	434	1,750	11,426

Unit: Percentage of regional total EDGAR Region	Copper	Zinc	Lead	Iron & Steel	H ₂ SO ₄	TOTAL
ED.A: CANADA	45.2	23.2	6.4	1.4	23.8	100.0
ED.B: USA	61.5	6.1	4.1	1.0	27.3	100.0
ED.C: LATIN AMERICA	77.2	7.3	2.1	1.1	12.4	100.0
ED.D: AFRICA	83.0	4.2	2.1	0.0	10.7	100.0
ED.E: OECD EUROPE	49.2	31.7	4.9	3.9	10.3	100.0
ED.F: EASTERN EUROPE	61.4	17.0	3.3	4.0	14.3	100.0
ED.G: CIS (FORMER USSR)	54.9	18.4	3.1	4.4	19.1	100.0
ED.H: MIDDLE EAST	82.7	0.0	1.5	3.3	12.6	100.0
ED.I: INDIA REGION	17.7	22.2	2.1	6.5	51.5	100.0

Table A.3.3.5. SO₂ Emissions from the Industrial Processes Source Category in 1990

ED.J: CHINA REGION	44.6	29.3	3.8	5.8	16.5	100.0
ED.K: EAST ASIA	62.6	27.0	1.9	4.0	4.4	100.0
ED.L: OCEANIA	52.3	35.3	6.3	1.9	4.1	100.0
ED.M: JAPAN	30.9	10.8	1.1	34.7	22.5	100.0
TOTAL	58.5	18.9	3.4	3.8	15.3	100.0

Unit: Percentage of source total						
EDGAR Region	Copper	Zinc	Lead	Iron & Steel	H ₂ SO ₄	TOTAL
ED.A: CANADA	0.7	1.1	1.7	0.3	1.4	0.9
ED.B: USA	9.2	2.8	10.5	2.3	15.7	8.8
ED.C: LATIN AMERICA	19.8	5.8	9.1	4.3	12.2	15.0
ED.D: AFRICA	9.4	1.5	4.1	0.0	4.6	6.6
ED.E: OECD EUROPE	16.4	32.8	28.5	19.9	13.2	19.6
ED.F: EASTERN EUROPE	6.9	5.9	6.4	6.9	6.1	6.6
ED.G: CIS (FORMER USSR)	20.0	20.7	19.6	24.7	26.6	21.3
ED.H: MIDDLE EAST	1.3	0.0	0.4	0.8	0.7	0.9
ED.I: INDIA REGION	0.3	1.1	0.6	1.7	3.3	1.0
ED.J: CHINA REGION	8.2	16.7	11.9	16.4	11.7	10.8
ED.K: EAST ASIA	4.9	6.5	2.6	4.8	1.3	4.6
ED.L: OCEANIA	1.9	4.0	4.0	1.1	0.6	2.1
ED.M: JAPAN	1.0	1.0	0.6	16.7	2.7	1.8
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0

Unit: Percentage of global total						
EDGAR Region	Copper	Zinc	Lead	Iron & Steel	H ₂ SO ₄	TOTAL
ED.A: CANADA	0.4	0.2	0.1	0.0	0.2	0.9
ED.B: USA	5.4	0.5	0.4	0.1	2.4	8.8
ED.C: LATIN AMERICA	11.6	1.1	0.3	0.2	1.9	15.0

Table A.3.3.5. SO₂ Emissions from the Industrial Processes Source Category in 1990

ED.D: AFRICA	5.5	0.3	0.1	0.0	0.7	6.6
ED.E: OECD EUROPE	9.6	6.2	1.0	0.8	2.0	19.6
ED.F: EASTERN EUROPE	4.0	1.1	0.2	0.3	0.9	6.6
ED.G: CIS (FORMER USSR)	11.7	3.9	0.7	0.9	4.1	21.3
ED.H: MIDDLE EAST	0.7	0.0	0.0	0.0	0.1	0.9
ED.I: INDIA REGION	0.2	0.2	0.0	0.1	0.5	1.0
ED.J: CHINA REGION	4.8	3.2	0.4	0.6	1.8	10.8
ED.K: EAST ASIA	2.9	1.2	0.1	0.2	0.2	4.6
ED.L: OCEANIA	1.1	0.8	0.1	0.0	0.1	2.1
ED.M: JAPAN	0.6	0.2	0.0	0.6	0.4	1.8
TOTAL	58.5	18.9	3.4	3.8	15.3	100.0

Table A.3.3.6. SO₂ Emissions from the Land Use Source Category in 1990

Unit: Gg S/yr EDGAR Region	Deforestation & savannah burning	Agricultural Waste	Total
ED.A: CANADA	0	26	26
ED.B: USA	0	105	105
ED.C: LATIN AMERICA	775	109	884
ED.D: AFRICA	1,624	118	1,742
ED.E: OECD EUROPE	0	105	105
ED.F: EASTERN EUROPE	0	25	25
ED.G: CIS (FORMER USSR)	0	121	121
ED.H: MIDDLE EAST	0	95	95
ED.I: INDIA REGION	59	300	359
ED.J: CHINA REGION	47	157	205
ED.K: EAST ASIA	90	83	173
ED.L: OCEANIA	0	12	12
ED.M: JAPAN	0	6	6
TOTAL	2,596	1,263	3,859

Unit: Percentage of regional total EDGAR Region	Deforestation & savannah burning	Agricultural Waste	Total
ED.A: CANADA	0.0	100.0	100.0
ED.B: USA	0.0	100.0	100.0
ED.C: LATIN AMERICA	87.7	12.3	100.0
ED.D: AFRICA	93.2	6.8	100.0
ED.E: OECD EUROPE	0.0	100.0	100.0
ED.F: EASTERN EUROPE	0.0	100.0	100.0
ED.G: CIS (FORMER USSR)	0.0	100.0	100.0

Table A.3.3.6. SO₂ Emissions from the Land Use Source Category in 1990

ED.H: MIDDLE EAST	0.1	99.9	100.0
ED.I: INDIA REGION	16.4	83.6	100.0
ED.J: CHINA REGION	23.2	76.8	100.0
ED.K: EAST ASIA	52.1	47.9	100.0
ED.L: OCEANIA	0.0	100.0	100.0
ED.M: JAPAN	0.0	100.0	100.0
TOTAL	67.3	32.7	100.0

Unit: Percentage of source total			
EDGAR Region	Deforestation & savannah burning	Agricultural Waste	Total
ED.A: CANADA	0.0	2.0	0.7
ED.B: USA	0.0	8.3	2.7
ED.C: LATIN AMERICA	29.9	8.6	22.9
ED.D: AFRICA	62.6	9.3	45.1
ED.E: OECD EUROPE	0.0	8.3	2.7
ED.F: EASTERN EUROPE	0.0	2.0	0.7
ED.G: CIS (FORMER USSR)	0.0	9.6	3.1
ED.H: MIDDLE EAST	0.0	7.5	2.5
ED.I: INDIA REGION	2.3	23.8	9.3
ED.J: CHINA REGION	1.8	12.5	5.3
ED.K: EAST ASIA	3.5	6.6	4.5
ED.L: OCEANIA	0.0	0.9	0.3
ED.M: JAPAN	0.0	0.5	0.2
TOTAL	100.0	100.0	100.0

Unit: Percentage of global total			
EDGAR Region	Deforestation & savannah burning	Agricultural Waste	Total

Table A.3.3.6. SO₂ Emissions from the Land Use Source Category in 1990

ED.A: CANADA	0.0	0.7	0.7
ED.B: USA	0.0	2.7	2.7
ED.C: LATIN AMERICA	20.1	2.8	22.9
ED.D: AFRICA	42.1	3.1	45.1
ED.E: OECD EUROPE	0.0	2.7	2.7
ED.F: EASTERN EUROPE	0.0	0.7	0.7
ED.G: CIS (FORMER USSR)	0.0	3.1	3.1
ED.H: MIDDLE EAST	0.0	2.5	2.5
ED.I: INDIA REGION	1.5	7.8	9.3
ED.J: CHINA REGION	1.2	4.1	5.3
ED.K: EAST ASIA	2.3	2.2	4.5
ED.L: OCEANIA	0.0	0.3	0.3
ED.M: JAPAN	0.0	0.2	0.2
TOTAL	67.3	32.7	100.0

1. Emission Database for Global Atmospheric Research (EDGAR) (Baars et al., 1991; Berdowski, 1992; Olivier et al., 1994).

Regional Inventories in the GEIA Version 1 Sulfur Inventories

CORINAIR-EMEP Pacyna Tonooka

Longitude

Figure 1

Figure 2

APPENDIX B

GLOBAL NATURAL SULFUR EMISSIONS

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B.1 SEA SPRAY

B.1.1 Introduction

Older estimates of natural S emissions to the atmosphere tended to include estimates of S emissions in particulate and aerosol forms, such as in sea spray (e.g., Kellogg et al., 1972; Ryaboshapko, 1983), whereas such non-gaseous emission sources tend to be absent from more recent estimates (e.g., Bates et al., 1992; Spiro et al., 1992).

This appendix includes sea salt aerosols as a natural S emission source because they are important in-atmosphere processors of gases. For example, Graedel et al. (1993) note that

"Emission inventories for HCl...are dwarfed by estimates that HCl volatilization from sea salt may be as much as 100-400 Tg/yr [Singh and Kasting, 1988; Möller, 1990], perhaps a hundred times the anthropogenic source on a global basis."

Overall, marine aerosols act as CCN (e.g., Woodcock, 1957) and they perform in-atmosphere processing of atmospheric gases, such as O_3 , NO_x , SO_x , and HCl (e.g., Eriksson, 1955; Robbins et al., 1959; Finlayson-Pitts, 1983; Möller, 1990), as well as methane and the three primary NMHCs, OH, plus byproducts of fossil fuel combustion, e.g., H_2 , HO_2 , and H_2O_2 (Singh and Kasting, 1988).

B.1.2 Estimates of Atmospheric Sea Spray Sulfate

Early estimates of the amount of salt that oceans put into the atmosphere were around 1 billion metric tons/yr (e.g., Eriksson, 1960; Kellogg et al., 1972). Assuming that generation of sea spray does not involve no elemental fractionation, 7.68% of the mass of salt in sea spray is S as sulfate (Mason,

1966, pp. 194).

Early estimates of flux of sea salt to the atmosphere used a limiting assumption that both water evaporated from oceans and sea spray aerosol generation have the same ratios of continental to oceanic deposition and that continental deposition accounts for approximately 10% of both. One hundred percent of sea salt redeposited to the oceans (e.g., Junge and Gustafson, 1957) and 1/3 deposited to land was assumed to be in the form of wet deposition (e.g., Eriksson, 1960).

However, in subsequent decades it became apparent that sea salt aerosol generation was actually much greater than earlier estimates. By the early 1980s, estimates of flux of sea salt to the atmosphere were increased to approximately 3-6 billion metric tons/yr (e.g., Meszaros, 1982; Varhelyi and Gravenhorst, 1983). By the early 1990s, reviews of the literature show that estimates of sea salt aerosol generation go up to 30 billion metric tons/yr; recent estimates are more near 10 billion metric tons/yr (Möller, 1990; Genthon, 1992). Thus, recent estimates of atmospheric sea salt indicate that the oceans emit approximately 800 Tg S/yr to the atmosphere as marine sulfate.

The older 1 billion metric tons sea salt/yr estimates assumed sea salt aerosols are ≤ 10 microns in diameter and wet deposition accounts for 1/3 of the land-deposited sea salt and 100 percent of ocean-deposited sea salt (Junge and Gustafson, 1957; Eriksson, 1960). Today's much larger atmospheric sea salt estimates assume that wet deposition accounts for 1/3 of land-deposited sea salt and only 5-10 percent of ocean-deposited sea salt, the rest being dry deposition (Möller, 1990). The newer estimates are also greater because they tend to recognize that appreciable amounts of salt aerosol are transported as > 10 micron particles. Recognition of long-distance transport of larger sea salt particles

comes in part from studies of particle size-distribution of trans-oceanic transport of African and Asian dust (e.g., Chester *et al.*, 1971; Talbot *et al.*, 1986; Genthon, 1992).

The following indicates that even the new estimates of flux of sea salt to the atmosphere may still underestimate flux of sea salt to the atmosphere. It is generally assumed that sea salt aerosols are principally concentrated below the boundary layer, however, quantitative chemical analyses reported as the standard tropospheric aerosol up to 9.1 km altitude (U.S. STANDARD ATMOSPHERE, 1976) show that 56 percent of the mass of aerosol chlorine is above the boundary layer.

B.2 MARINE S GAS EMISSIONS

Seawater is an extremely sulfur-rich growth medium with an average SO_4^{2-} concentration of some $2,650 \text{ mgL}^{-1}$ (Mason, 1966, pp. 194): approximately 1,000 times the SO_4^{2-} concentration of typical sulfate-rich acid rain. Accordingly, not only does airborne sea spray introduce significant amounts of S into the atmosphere, waste gases emitted by marine and coastal organisms are also particularly sulfur rich. For example, analyses across freshwater/salt water gradients, as well as comparison of freshwater to salt water ecosystems, show that biological hydrocarbon gas emissions predominate in freshwaters and biological S gas emissions increase with increasing SO_4^{2-} concentrations at the expense of decreasing hydrocarbon emissions (e.g., Reeburgh and Heggie, 1977; Bartlett *et al.*, 1985; Levanthal, 1991).

Because marine and coastal ecosystems cover about 70 percent of the earth's surface, biological gas emissions from marine and coastal microorganisms are considered to be by far the largest natural source of S gas emissions to the

atmosphere (Bates *et al.*, 1992; Spiro *et al.*, 1992).

Estimates of global S emissions from oceans (and their coastal boundaries) implicitly, if not explicitly, assume constancy in nature. Nevertheless, research clearly shows that changes in chemical and physical conditions can potentially create measurable variation in S emissions. As will be subsequently discussed, this may in part account for the wide range in published estimates of marine S gas emissions 11.8 (Spiro *et al.*, 1992) to 54 Tg S/yr (Andreae, 1990).

B.2.1 Anthropogenic Influence

While freshwater primary productivity is principally phosphorus (P) limited (e.g., Schindler, 1977), the principal limiting macronutrient in salt waters is nitrogen (followed in importance by silica and P, where P is limiting largely to the degree that P affects nitrogen-fixing organisms (e.g., McElroy, 1983; Rosenberg, 1985; Davies, 1990)).

Globally, anthropogenic N-fixing activities are estimated to have approximately doubled the annual amount of biologically available N (Kinzig and Socolow, 1994). Significant increase in global levels of fixed nitrogen by human activity has raised a number of concerns. The particular concern which is of interest in this appendix is similar to that raised in the 1960s and 1970s about P and eutrophication of freshwater ecosystems, namely, N eutrophication of salt water ecosystems.

Given the importance of N for marine productivity, concern has been raised (both in public and scientific publications) that increases of biologically available N to oceans -- both in the form of atmospheric deposition (popularly called acid rain) and surface runoff (principally N from fertilizer) -- has resulted in significant eutrophication of coastal and near-ocean regions (e.g.,

Paerl, 1985; Rosenberg, 1985; Wulff and Rahm, 1988; Turner and Rabalais, 1991; Newsweek, 1988; The Universal Almanac 1991, 1990).

In order to assess whether anthropogenic stimulation of primary productivity (eutrophication) significantly influences biogenic salt water S gas emissions, it is important to determine the overall efficiency of primary productivity in producing S gases.

Estimated values for salt water primary productivity of 19,000 and 40,000 Tg C/yr were reported (Ryther, 1969; Bolin *et al.*, 1987). Also reported were the prominent estimated values of biogenic marine emissions of S gases to the atmosphere of 11.9 and 15.4 Tg S gases/yr (Bates *et al.*, 1992; Spiro *et al.*, 1992).

The above data indicate that approximately 1,200 to 3,400 g C primary productivity is reported to emit 1 g S gases. This range in values for biogenic marine S gas emissions was used to estimate whether anthropogenic fertilization of salt water ecosystems has significantly influenced salt water biogenic emissions of S gases to the atmosphere.

However, before proceeding, it is important to note that new studies are still adding to our inventory of marine primary productivity (e.g., Arrigo and McClain, 1994; Fritsen *et al.*, 1994). This is continuing the past trend of increasing estimates of marine primary productivity (e.g., compare Ryther (1969) to Bolin *et al.* (1987)). Continuation of this upward trend in estimates of background marine primary productivity can be expected to cause downward revision of future estimates S gas emitted per unit of marine primary productivity stimulated by anthropogenic N.

Additional ecologically-based caveats showing that estimates of marine S gas emissions stimulated by N fertilization tend to be high will be discussed in

sections B.2.1.1 and B.2.1.2.

B.2.1.1 - Nitrogen Fertilization by Runoff

World agricultural productivity was N limited until after the Haber-Bosch process was developed which converts atmospheric nitrogen gas (N_2) into plant-usable form. However, even in the United States, chemical N fertilizer was not used in appreciable amounts until well after World War II (Russell and Williams, 1977; Viets, 1977; Turner and Rabalais, 1991).

Few credible efforts have been made to quantify eutrophication of salt water ecosystems by anthropogenically enhanced N in runoff (e.g., Rosenberg, 1985; Wulff and Rahm, 1988; Turner and Rabalais, 1991). Furthermore, only the Mississippi Basin study by Turner and Rabalais (1991) was found to even begin to approach the time-frame or range of conditions needed for global extrapolation. The Mississippi basin has nearly the full range of land-use activities containing both the U.S. industrial heartland and its breadbasket. It also contains nearly the full range of global agricultural and land-use activities: boreal forest to irrigated arid lands/sparse rangelands to rice/sugarcane subtropical units.

The Mississippi River watershed covers 41 percent of the contiguous 48 states. "In terms of length, discharge, and sediment yield the main river channel is the third, eight, and sixth, respectively, largest river in the world (Milliman and Meade, 1983).

"Forty-two percent of the nitrogen fertilizer... used annually in the United States from 1981 to 1985 was applied in states that are partially or completely in the Mississippi River watershed...." (Turner and Rabalais, 1991).

The nitrogen content of Mississippi River water entering the Gulf of Mexico

remained essentially constant from 1905 to the 1950s. After the 1950s, the Mississippi's N load to the Gulf doubled, peaking around 1980 (Turner and Rabalais, 1991).

The mean 1981-1987 annual N loading to the Gulf of Mexico was calculated to be 130.3×10^6 kg N, double that of 1954-1959 (the latter considered background N level). Thus, the increase of N loading to the Gulf by the Mississippi was concluded to be 65,150 metric tons N/yr over background. Recent N loading to the Gulf is 53% nitrate, 43% organic N, and the remainder in miscellaneous forms (Turner and Rabalais, 1991).

Using the standard C/N ratio of 6.75 for marine algae and assuming that N is recycled 3.7 times per year by marine algae (Turner and Rabalais, 1991), it is predicted that the estimated 4.33×10^6 metric tons N fertilizer used annually in the Mississippi basin (42% of the United States' 10.31×10^6 metric tons N/yr) increased marine algae productivity in the Gulf of Mexico by 1.6×10^6 metric tons C/yr.

Thus, the Mississippi basin/Gulf of Mexico study indicates that on average, for each metric ton/yr of N fertilizer used in the Mississippi basin¹,

¹Chemical fertilizer is defined as representing all sources of increased N in runoff (Turner and Rabalais, 1991). However, this definition includes other significant sources of increased N in runoff: N-fixed by legumes; combustion of fossil fuels; and ecosystem recovery from land-use change. Regarding legumes, agronomists have increased the use of N-fixing legumes as well as improved their N-fixing ability by inoculating legume seeds with new strains of N-fixing rhizobium bacteria more efficient than naturally found in soils (Edmund et al., 1964, pp. 110). Overall, N-fixation by legumes has quickly grown to be twice that produced by fossil fuel combustion and other industrial activities (Kinzig and Socolow, 1994). This is quite impressive in the face of the statistic that in North America (as well as worldwide), N-fixation by fossil fuel combustion and other industrial activities has more than doubled between 1950 and 1980 (Dignon and Hameed, 1989). Also, N in runoff has probably also increased due to landscape recovery from earlier widespread disturbance (Vitousek, 1977; Krug, 1991). In summary, N runoff from "chemical fertilizer" is, by definition, simply runoff of anthropogenic N to the world's oceans.

approximately 0.38 metric tons of marine algae C/yr are produced.

Extrapolating the Mississippi Basin/Gulf of Mexico system to world N fertilizer usage, and assuming that S emitting marine algae are stimulated in direct proportion to overall enhanced primary productivity, Table B.1 summarizes the results of these calculations for runoff N enhancement of global marine C and resultant enhanced marine S gases emission.

Table B.1 shows that maximum estimated stimulation of marine S gas emissions from enhanced global runoff of dissolved N to the oceans appears to be negligible. The estimated historical maximum of 25,000 metric tons S/yr (Table B.1) is extremely small compared to the generally accepted estimates of natural global emissions (Table B.2).

B.2.1.2 - Nitrogen Fertilization by Atmospheric Deposition

Defining the atmospheric flux of anthropogenic N to the world's oceans from fossil fuel combustion is analogous to defining N runoff from chemical fertilizer. While useful (and actually necessary in lieu of additional research), such definition necessarily simplifies a much more complex situation. Typically, measurements are made of atmospheric transport of NO_x from land to ocean and reported as a percentage of estimated NO_x emitted from combustion processes (e.g., Galloway and Whelpdale, 1987). Nevertheless, other human activities (such as fertilization of landscapes and ecosystem disturbance) also influence NO_x emissions, however indirectly (e.g., Ryden et al., 1984; Livingston et al., 1988; Wessman et al., 1988; Coyne et al., 1994; Robertson, 1994). While, qualitatively, such indirect anthropogenic enhancement of natural N emission by factors such as N fertilization has probably increased in time (as have N emissions from fossil fuel combustion), no such credible quantitative estimates

of these indirect anthropogenic N emissions appear to exist. Therefore, it is difficult to ascertain if such indirect anthropogenic enhancement of N emissions is significant relative to N emitted from fossil fuel combustion.

In lieu of such quantitative data, it is assumed that indirect anthropogenic N emissions maintain the same proportionality to fossil fuel emissions through time and space, especially as regards atmospheric deposition of anthropogenic N to the world's oceans.

For 1980, Levy II and Moxim (1989) calculated that flux of anthropogenic N emissions to the world's oceans was 4.5 Tg. This estimate was verified by measurements of N flux to the Atlantic and Pacific oceans both before and after their study was completed (e.g., Galloway and Whelpdale, 1987; Levy II and Moxim, 1988; 1989; Prospero and Savoie, 1989).

To develop estimates of enhanced marine primary productivity and marine S₂ gas emissions from atmospheric deposition of anthropogenic N (Table B.3), the following information is used:

- The standard C/N ratio is 6.75 for marine algae;
- N is recycled 3.7 times per year (Turner and Rabalais, 1991);
- 1980 proportionality between total anthropogenic N emissions and oceanic deposition is constant over time; and
- S₂ gas emissions are directly proportional to increased primary productivity.

Even though global anthropogenic N emissions are only 1/6th the amount of anthropogenic N fixed for agriculture (Kinzig and Socolow, 1994), atmospheric deposition of anthropogenically-fixed N is far more effective than agricultural N in enhancing marine primary productivity and marine S₂ gas emissions (Tables B.1 and B.3). As previously discussed, the ocean receives little of agriculturally applied nitrogen. Even so, the maximum estimates of enhanced global marine

primary productivity and enhanced marine S gas emissions by atmospheric deposition are negligible on nature's global scale (i.e., 117 versus 19,000-40,000 Tg C/yr and 0.098 versus 11.9-15.4 Tg S gases/yr). Combined maximum runoff plus atmospheric N stimulation (Tables B.1 and B.3) is likewise negligible (i.e., 147 versus 19,000-40,000 Tg C/yr and 0.121 versus 11.9-15.4 Tg S gases/yr).

Atmospheric stimulation of marine S gas emissions may be overestimated. Algae prefer to manufacture various N compounds (osmolytes) to regulate an osmotic balance between cell solution and surrounding salt water. Unlike coastal waters, much of the open ocean is very low in N content. In such low N waters, species of algae which can produce the osmolyte DMSP (a metabolic precursor of DMS) are favored. Indeed, reducing N concentrations in sea water stimulates even greater DMSP production by DMSP-producing algae (Andreae, 1986). Thus, N deposition may actually decrease marine DMS production.

B.2.1.3 - Other Anthropogenic Factors

B.2.1.3.1 - Phosphorus

Data on change of anthropogenic flux of phosphorus to the oceans are scarce. While there has been the occasional hypothesized effect of anthropogenic influences on marine eutrophication (e.g., Kump, 1988), enhancing marine primary productivity, only the following general statement by Kaula (1990) has been found in the literature:

"the flux of phosphorus from land to oceans has approximately doubled relative to preindustrial times..."

Little information exists to develop a model of the quantitative effect of enhanced phosphorus flux on marine emissions of S gases.

B.2.1.3.2 - Erosion

Sediment is well known as an importance nutrient source for marine ecosystems. While earlier land-use practices were highly erosional (and may still be in developing nations), the principal effect of industrialization/modernization on river sediment loads to the oceans is to reduce these loads.

For example, the creation of the Mississippi Delta (and its maintenance against marine erosion and subsidence from dewatering sediments) is the result of naturally high rates of erosion over the last 6,000 years (Kesel, 1988).

However, since European settlement of the Mississippi Basin, the amount of sediment that the basin deposits to the Gulf of Mexico has declined by some 540 million metric tons/yr from its natural level, from 141×10^6 to 681×10^6 metric tons/yr since 1851 (Table B.5). The consequence of this drastically reduced rate of sediment supply is that, as Kesel (1988) noted, the "rate of land loss along the Louisiana coast has increased from 17 km²/yr in 1913 to 102 km²/yr in 1980."

This pattern of reduced sediment discharge is seen for the United States as a whole. For example, by the 1960s, the rate of sediment discharged by all rivers in the United States (Curtis et al., 1973) was less than that naturally discharged by the Mississippi alone (Kesel, 1988). The U.S. pattern of reduced sediment yield applies generally to the land-use and conservation practices of developed countries. For example, study of the sediment loads of the world's rivers reveals that European rivers now have exceptionally low sediment loads (Milliman and Meade, 1983).

Sediment loads of a number of major rivers in developing nations have also undergone significant reduction. For example, the Orange River (the major river draining the countries in southern Africa) had a sediment discharge of 153×10^6

tons/yr around 1930 which dropped to 17×10^6 tons/yr by 1969 (Rooseboom and Harmse, 1979; Milliman and Meade, 1983). The major river in east Africa, the Zambesi, has had its sediment load decreased from 48×10^6 tons/yr to $<20 \times 10^6$ tons/yr by construction of dams (Milliman and Meade, 1983). Similarly, the Nile River, with the completion of the high Aswan Dam, has had its sediment discharge go from 110×10^6 tons/yr to less than 10^6 tons/yr (Milliman and Meade, 1983). Decreased nutrient loading by Nile sediment has resulted in declining Mediterranean fisheries as well as enhanced areal losses of the Nile delta (Milliman and Meade, 1983; Stanley and Warne, 1993), the latter also observed for the Mississippi. In India, the Indus River appears to have undergone sediment load reduction even greater than that observed for the Mississippi, with sediment to the ocean down to only 100×10^6 tons/yr (Milliman and Meade, 1983).

Overall, some 70 percent of the sediments delivered to the oceans by the world's rivers come from the watersheds of "southern Asia and the larger islands in the Pacific and Indian Oceans, where sediment yields are much greater than for other drainage basins" (Milliman and Meade, 1983). However, research on the pristine watersheds of the Southern Alps of the west coast of New Zealand (Griffiths, 1979), as well as research in Taiwan, the latter having the highest rates of erosion in the world (Li, 1976), indicate that the exceptionally high rates of erosion for this part of the world are principally natural (Milliman and Meade, 1983).

Thus, the overall global effect of human activity on sediment yields to marine ecosystems is ambiguous. It is difficult to say whether the net impact of the anthropogenic activity on world river sediment yields to marine ecosystems over the last 145 years has significantly increased or decreased marine primary productivity and, thereby, natural marine emissions of S gases. To quote from

the review of Milliman and Meade (1983):

[T]oday's river sediment loads are strikingly affected by man...The tremendous sediment loads transported by the Yellow and Ganges/Brahmaputra Rivers are at least partly due to poor soil management...More recently, sediment loads have been decreased drastically by the construction of reservoirs...In some river basins, man-made changes have been made recently enough that the data can be adjusted to obtain some indication of natural conditions. In other river basins (those in India and China, for example), any indicators of natural conditions have been obscured for millennia."

However, it can be said that in recent geologic times natural variations in the rate of sediment deposition to ocean basins considerably exceed any possible modern anthropogenic influence due to the large amount of sediments deposited to oceans by ice age glaciers and their meltwaters and also by massive aeolian inputs during the last ice age (e.g., Damuth and Fairbridge, 1970; Parmenter and Folger, 1974). To quote Milliman and Meade (1983):

"Present-day climates and erosional regimes do not resemble even those of a few thousand years ago, and glacial rivers in particular have been more numerous during glacial epochs." [glacial rivers had extraordinarily large sediment loads.]

Anthropogenic eutrophication of marine ecosystems appears to be perceived as greater than it actually may be because marine basin eutrophication and its associated fishkills, red tides, and even anoxia, are unusual and, therefore perceived as being unnatural.

Similar to the problem of lake acidification, when one looks at natural- and human history, one sees that a portion of the problem assigned to human activities is actually natural (Lefohn and Krug, 1990). For example, human activity is assigned the blame for anoxia of the Black Sea basin. Nevertheless, today's anoxia is but one over many similar anoxic episodes which have prevailed in the Black Sea basin over the last 6,000 years (Sinninghe Damste et al., 1993). Also research results show that modern episodes of anoxia phenomena in the Gulf

of Mexico, the West Coast, and elsewhere -- now popularly attributed to modern human activities -- were recorded by the very earliest observers centuries earlier (e.g., Meyer et al., 1928; Connell and Cross, 1950; 1951).

In summary, it is unclear what the net global effect of anthropogenic activities since 1850 has had on net global sediment loads to the oceans. Accordingly, estimates of marine S gas emissions stimulated by net anthropogenic effects on erosion have not been made.

B.3 NATURAL VARIATION IN S GAS AND SEA SPRAY EMISSIONS

B.3.1 - Influence of climate on Marine S Gases

While a number of volatile sulfur gases are produced biologically and photochemically in marine environments (e.g., Andreae, 1986, 1990; Bates et al., 1992), dimethyl-sulfide (DMS) is by far the most prominent gas and is the prime source of non-sea salt (nss) sulfate. Indeed, DMS is so prominent that estimates of marine S gas emissions often only include DMS (e.g., Berresheim, 1987; Bates et al., 1992; Spiro et al., 1992). Similarly, studies of marine S gas emissions preserved in ice cores of the world's ice caps (Greenland and Antarctica) focus on marine DMS emissions vis-a-vis DMS' partial oxidation product (MSA) and nss sulfate, the endproduct of in-atmosphere DMS oxidation.

Ice cores from both the Greenland and Antarctic high plateau ice sheets show that emissions of marine S gases are very climate sensitive. These cores, as pointed out by Legrand et al. (1991), "confirm that the ocean-atmosphere sulfur cycle is extremely sensitive to climate change." These ice cores show that average levels of both MSA and nss sulfate, in both the northern and southern hemispheres, have undergone abrupt, marked, and complex changes with climate. Values of MSA and/or nss sulfate -- that have been sustained for

centuries or millennia -- abruptly change with climate change; and these changes are often 5-fold for both hemispheres. Furthermore, these new and greatly different levels of marine S are then often sustained for centuries or millennia (Saigne and Legrand, 1987; Legrand et al., 1991; Hansson and Saltzman, 1993).

A high resolution 70-year analysis of an ice core taken on the high altitude (~3,000 m above msl) Antarctic Plateau near the South Pole has been performed, which is useful for estimating changes in natural marine S gas emissions (Legrand and Feniet-Saigne, 1991) for part of the time frame of this assessment.

This high resolution ice core shows rapid and large variations of MSA (2 to 60 ng/g) accompanied by lesser magnitude (fractional to 3-fold) variations in nss sulfate (Legrand and Feniet-Saigne, 1991). Peak rates of deposition revealed in the ice core not only coincide with the El Niño events, they also coincide with El Niño intensity and duration (Legrand and Feniet-Saigne, 1991).

Deposition of MSA and nss sulfate has been determined to be non-local: to be long-distance and general transport from mid- and low-latitudes (e.g., Legrand et al., 1991; Legrand and Feniet-Saigne, 1991; Legrand et al., 1992; Hansson and Saltzman, 1993). Its episodes of increased quantity may be due to a number of factors operating jointly or separately over various geographic regions, such as:

- enhanced marine primary productivity;
- N impoverishment by thermal stratification favoring DMS production as an osmolyte;
- increased windiness enhancing gas transfer of DMS from seawater to air;
- increased turbulence increasing algae cell damage and concomitant DMS release to sea water; and
- enhanced atmospheric circulation (Andreae, 1986; Saigne and Legrand, 1987; Komhyr et al., 1991; Legrand and Feniet-Saigne, 1991; Legrand et al., 1991; 1992; Spiro

et al., 1992; Hansson and Saltzman, 1993).

Table B.6 provides estimates of marine S emissions based on the high resolution marine S ice core data using the following assumptions:

1. El Niño influences the climate (and thus marine S gas emissions) of only the Southern Hemisphere; and
2. Marine S values in the ice core are directly proportional to marine S emissions.

Assumption 1 underestimates the effect of El Niño on marine processes because El Niño also significantly influences the climate of the Northern Hemisphere (e.g., Bradley et al., 1987; Kumar et al., 1994). However, since comparable Northern Hemisphere ice core data have not been studied, the El Niño effect will be assumed to operate in only the Southern Hemisphere. Assumption 2 overestimates the El Niño stimulation of marine emissions because El-Niño-enhanced circulation probably increases the proportion of marine gases carried by long-distance transport (e.g., Komhyr et al., 1991). Finally, the range of estimates of the El Niño effect on the DMS portion of marine S gas emissions are based on the background estimates of Bates et al. (1992), 8.8 Tg S/yr, and Spiro et al. (1992), 6.5 Tg S/yr, of Southern Hemisphere marine DMS emission north of 65°S latitude.²

Based on these data and assumptions, note that mean estimate of DMS marine S gas emission induced by El Niño is 33.6 Tg S/yr for the 13 El Niños recorded

²Proportion of total Southern Hemisphere to 65°S and south marine DMS emission data of Bates et al. (1992) have been used to proportionately adjust Spiro et al. (1992) data to exclude DMS emissions south of 65°S: that latitude which roughly corresponds to the southern limit of open ocean around Antarctica (Weyant, 1966). Winter ice goes out to ~65°S, approximately doubling the area of Antarctica to 30 million km². For the most part, at full sea ice cover, open ocean lies nearly 3,000 km from the Antarctic interior (Weyant, 1966; Markov et al., 1970). Accordingly, ocean south of 65°S latitude is considered "local" ocean whose DMS emissions essentially do not make it up to be deposited in the ice of the high plateau of the Antarctic interior.

in Antarctic ice since 1928 compared to the background estimates of 6.5 to 8.8 Tg S/yr. For two El Niño events, marine S gas emission can be enhanced up to some 80 Tg S/yr above estimated background, an amount which approaches total anthropogenic S emissions.

Clearly the effect of climatic fluctuations on marine S gas emissions is potentially very large and merits significant additional attention. Significant additional research is needed not only in refining the accuracy of prediction, but in also using the El Niño history (e.g., Quinn et al., 1987) to develop and further refine estimates of El-Niño-induced variation in marine S gas emissions of the historic past.

Finally, the spread in published estimates of global marine DMS emission is large: at least from 11.9 (Spiro et al., 1992) to 54 Tg S/yr (Andreae, 1990). Spiro et al., 1992 report that the wide spread is largely due to differences in measured sea water DMS concentrations generalized to the sampled regions. Andreae (1986) notes that estimates of marine DMS emissions are also very sensitive to mean wind velocities.

In summary, concentrations of DMS in sea water vary greatly with time, being quite sensitive to climatic conditions. Also the flux of marine DMS is very sensitive to wind speeds. Accordingly, part, or even most, of this wide spread in estimates of marine S gas emissions may be real rather than modeling differences. That marine S gas emissions are highly sensitive to climate change is supported by the Antarctic ice core which shows that El Niño has a marked effect on rates of marine S deposition in Antarctica.

B.3.2 - Influence of Climate on Sea Spray

The rate that droplets of sea water are separated from the air-water

interface is a function of energy: energy being a function of wind velocity squared (v^2). The flux of sea spray increases exponentially with wind velocity (Blanchard and Woodcock, 1980). Higher wind speeds result in an exponential increase in the number of larger aerosols relative to smaller aerosols (Blanchard and Woodcock, 1980; Singh and Kasting, 1988).

The following analysis indicates that exponential growth in estimates of sea salt flux to the atmosphere may not only be due to improving models, but some portion of this increase may be real.

Comprehensive analysis of 1948 - 1972 meteorological data for the North Atlantic Ocean and the South Atlantic Ocean reported in the *Monthly Weather Review* show that surface wind velocities have been increasing over both oceans (Bunker, 1980). A more recent review published in *Nature* shows a similar trend of increasing velocity of surface winds over the Pacific Ocean. To quote from the review's abstract:

"We also show from the observations that, in the period 1950-81, there was a trend towards increasing trade winds over much of the Pacific Ocean. A similar trend has been observed in Atlantic Ocean data." (Whysall et al., 1987).

Furthermore:

"These [effects] would combine to give increased evaporation and therefore stronger convection in the ITCZ." (Whysall et al., 1987).

A subsequent review (Komhyr et al., 1991) supports the conclusion of enhanced circulation that strengthened Hadley Cell circulation in the equatorial region, associated with warmer SST's, enhances the transport of ozone-poor tropospheric air into the lower stratosphere, from where it is transported to higher latitudes. The authors also points out that

"[E]nhanced Hadley Cell circulation intensity when equatorial Pacific SSTs warm (29, 30) as they did in 1976-1987..., the flux into the stratosphere of...naturally occurring (ocean derived) chlorine and bromine compounds, is increased."

In summary, as climatic conditions change with time, so does flux of sea salt into the atmosphere. Woodcock's nomograph shows that a 2% increase in mean wind velocity increases flux of sea salt into the atmosphere by $\geq 10\%$ (Blanchard and Woodcock, 1980). Given that estimates of sea salt flux into the atmosphere are currently approximately 800 Tg S/yr, just a 2% increase in mean oceanic wind velocity will result in an increase of ≥ 80 Tg S/yr, an increase significant when compared to estimated total flux of anthropogenic S emissions.

In conclusion, small changes in average global climate may cause significant changes in the flux of atmospheric sea salt S into the atmosphere.

B.4. VOLCANIC EMISSIONS

Three of the major summaries of the global sulfur cycle estimate global volcanic S emissions at 9.3 Tg S/yr (Bates et al., 1992), 9.6 Tg S/yr (Spiro et al., 1992), and a median estimate of 28 Tg S/yr within an estimated range of 14 - 42 Tg S/yr (Ryaboshapko, 1983).

A more recent review of the literature shows that estimates of annual global SO₂ emissions from vulcanism vary 30-fold: from 0.75 Tg S/yr to 25 Tg S/yr (Bluth et al., 1993).

Estimates of gas emissions by both quiescent and explosive vulcanism, not only because of variability in vulcanism, can vary widely due to the methods of measurement and the assumptions that underlie these measurements and the estimates derived from them.

For example, Palais and Sigurdsson (1989), in Geophysical Monograph 52, estimate that the 1963 Agung eruption emitted 2.84 Tg H₂SO₄ based on composition and volume of erupting magma. However, estimates derived from ice core data obtained at a number of locations in Antarctica indicate that the Agung eruption

emitted approximately 30 Tg H_2SO_4 (Legrand and Delmas, 1987) -- a ~10-fold larger estimate. Optical measurements of stratospheric aerosols produced by the 1963 Agung eruption (optical measurements calibrated against stratospheric aerosol chemistry produced by the 1982 El Chichon eruption) indicate that the 1963 Agung eruption injected 10-20 Tg H_2SO_4 aerosol into the stratosphere (Rampino and Self, 1984). Thus, the estimates of the Agung S emission differ by an order-of-magnitude based on the method of estimation.

Another example of the wide range of estimates of volcanic S emissions comes from a recent publication on the Italian volcano, Stromboli (Allard et al., 1994). Stromboli is a continuously-erupting volcano. S emissions (as SO_2) from this best-known, best-researched volcano in the world (along with its neighbor Aetna) have recently been drastically revised upward to 10% (Allard et al., 1994) of the world's total volcanic S (as SO_2) emissions (Bluth et al., 1993).

Because many volcanic events are instrumentally unobserved, critical examination of the geologic literature shows that estimates of emissions even from observed volcanic events are necessarily educated guesses; rates of degassing and volumes and compositions of magmas being degassed are deductions, as much of the magmas are unseen. There are also appreciable gas/solid/liquid ejecta interactions, most reactions of which are necessarily inferred (e.g., Johnston, 1980; Rose et al., 1988; Allard et al., 1994).

But most known volcanoes and events are neither researched as well as the Agung eruption nor as thoroughly as Stromboli. It follows then that estimates of S emissions from most volcanoes are necessarily subject to an even greater uncertainty than the order-of-magnitude range observed currently.

Finally, while direct observations (e.g., Kerr, 1994) and the geologic record (e.g., Owen and Rea, 1985) both show that volcanic activity does vary with

time (the latter showing nearly order-of-magnitude variation), Simkin et al. (1981, pp. 22-26) show that measured changes in volcanic activity have a strong subjective component: measured volcanic activity increases with economic and scientific progress and decreases during times of civil and economic unrest. Thus, the above-mentioned uncertainties are compounded by subjectivity of observation.

In summary, estimates of annual volcanic S gas emissions fall within a 50-fold range: from 0.75 to 42 Tg S. The better known median estimates range from 9 to 24 Tg S/yr and these data suggest that the average annual value lies somewhere ≥ 9 Tg S.

B.5 OTHER TERRESTRIAL EMISSIONS

B.5.1 Wind-Blown Soil

Wind-borne soil material may be a significant natural source of terrestrial S emission. The earliest soil scientists recognized that gypsum (CaSO_4) is an important soil component. For example, the mid-1800s the German predecessors of modern soil science (the German school of agro-geology) classified soils into three groups based on their chemical composition:

1. - Silicate soils;
2. - Carbonate soils; and
3. - gypsum soils (Glinka, 1927, pp. 20).

With the advent of modern soil science being developed in the 1880s in Russia, Russian soil scientists began classifying world soils by process -- the interaction of soil-forming factors -- rather than classifying soils by chemical composition.

The Russian soil scientists recognized gypsum to be an important soil

component. Nineteenth century Russian soil scientists noted that gypsum was an important soil component in their classification of 2 of their 4 major world soil groups: soils of (1) steppe/forest and (2) semi-arid and arid regions (Glinka, 1927, pp. 31).

The prevalence of gypsum-bearing soils (gypsum co-occurs with both carbonates and salt) in various regional world soil types is also clearly seen in seminal modern soil science publications, such as Duchaufour's *Ecological Atlas of Soils of the World* (1978). It is in regions which contain gypsum-bearing soils (Duchaufour, 1978) in which most wind soil erosion occurs (e.g., Chepil, 1954; Smith et al., 1970; Jackson et al., 1973; Yaalon and Ganor, 1973).

Ryaboshapko's (1983) assessment, which is one of the most comprehensive on the role of the aeolian (wind-blown soil) S emissions in context of the global atmospheric sulfur budget, noted that

"Junge (1965) inferred the average concentration of sulphate in the atmosphere over continents to be $0.17 \mu\text{g S m}^{-3}$, while Friend (1973) estimated it to be $1.5 \mu\text{g S m}^{-3}$. Observations in dusty regions should be considered separately. The Soviet investigators Andreev and Lavrinenko (1968) and Khusanov et al. (1974) made measurements in Middle Asia in a region characterized by intensive aeolian weathering. In that region the soils are mainly sands, serozems, and saline soils. Saline soils with sulphate concentrations of up to 5% are known to have a loose structure and are capable of producing dust at wind speeds of $3\text{-}4 \text{ m sec}^{-1}$ (Zakharov, 1965). The average sulphate concentration of the atmosphere near Tashkent is $11.2 \mu\text{g S m}^{-3}$ according to Andreev and Lavrinenko (1968), and $10 \mu\text{g S m}^{-3}$ according to Khusanov et al. (1974). Both groups noticed that during dust-storms, concentrations increase drastically and reach almost $30 \mu\text{g S m}^{-3}$. This confirms the aeolian origin of sulphate in the atmosphere of this region.

Ryaboshapko (1983, pp. 222-223) has pointed out

"The data obtained in other arid zones of the world differ greatly from the results above. Penkett et al. (1979) reported values of $10 \mu\text{g S m}^{-3}$ for East Africa. Still lower concentrations were found by Hoffer et al. (1979) for deserts in the south-western USA. Increased sulfate concentrations were observed more than once in the atmosphere during transport of aerosols from Sahara to the Atlantic (Gravenhorst, 1978; Buchen and Georgii, 1971; Winkler, 1975), and

abnormally high deposition of sulphate from the atmosphere was observed in the arid zones of Australia (Hingston and Gailitis, 1976)."

Based on seasonality, areal distribution, mixing height and other factors, Ryaboshapko (1983) determined that annual global aeolian emissions of sulfate - S lie within the 3.3 to 10 Tg S/yr range; the average value being 6.7 Tg S/yr (Ryaboshapko, 1983, pp. 273-274).

Bates et al. (1992) estimated that aeolian S emissions are only 0.35 Tg S/yr. However, their assessment was reportedly based on only one study of wind-blown dust over the North Atlantic.

The estimate by Ryaboshapko's (1983) of aeolian sulfate - S emissions appears to be the most scientifically based and, therefore, may be the more accurate estimate. Aeolian S emissions appear significant for some, but not all, arid and semi-arid regions.

B.5.2 Fire

Estimates of annual flux of S emissions from biomass burning (fire) are approximately 2 Tg S/yr (e.g., 2.2 Tg S/yr Bates et al. (1992); 2.3 Tg S/yr Spiro et al. (1992)).

However, S emissions from biomass burning have appreciable uncertainty. Bates et al. (1992) point out that

"Since most burning area estimates are known no better than $\pm 50\%$ (Robinson, 1989), and there are few emission measurements for sulfur species, these estimates are expected to have considerable uncertainty."

Biomass burning to the degree that it involves human agency, is thought to be "unnatural." This common perception was well stated by Bates et al. (1992) when they noted that biomass burning "can not necessarily be considered a

'natural' sulfur emission since as much as 95% of global burning is thought to be human initiated..." However, in this appendix fire, including the human use of fire, is considered a natural source of S emission rather than an industrial one. Furthermore, aboriginal man has thoroughly shaped the world's terrestrial ecosystems for millennia through the use of fire. Thus, as we shall see, anthropogenic pyric influence is an integral part of the natural world.

Pre-Industrial societies make extensive use of fire in manipulating their environment whereas a major thrust of industrial/scientific societies is the development of social and technological instruments to replace wildfire as a prime provider of our needs. The rest of this section's discussion is made to support this far-reaching and important conclusion. The so-called pristine landscapes of the world are anthropogenic artifacts created by aboriginal man. For example, with but few exceptions (such as the northern spruce/fir forest, Krug and Frink (1983)), the ecosystems encountered by European explorers of the New World were not mature (climax), undisturbed ecosystems. Indeed, whole ecologies -- from the Douglas fir forests and the redwood forests of the West - to the grasslands of the interior - to the pine forests of the east coast -- literally owe their existence to the interference of pre-historic Native Americans with fire.

To quote a review from *Scientific American*:

"Before Europeans came to North America, fires periodically swept over virtually every acre on the continent which had anything to burn...Most prehistoric fires were undoubtedly the work of man."

"Notwithstanding the popular conception, American Indians were not cautious in using fire. They did not conscientiously put out camp fires nor, unless their villages were threatened, did they try to keep fires from spreading. Often they burned intentionally -- to drive game in hunting, as an offensive or defensive measure in warfare, or merely to keep the forest open to travel...In the narratives of the explorers of North America are numerous accounts of traveling for days through smoke from distant fires, and the

passing through burned-over prairies and woodlands." "Most ecologists believe that a substantial portion of North American grasslands owe their origin and maintenance to fire...[In the absence of destructive fires being set by Native Americans] [l]arge parts of these grasslands are now being usurped by such shrubs as mesquite, juniper, sagebrush and scrub oak. Mesquite alone has spread...until it now occupies about 70 million acres of former grassland." (Cooper, 1961).

Overall it can be said that

"Indian burning in the United States was almost universal. An undoubtedly incomplete review of the literature brought to light more than 200 references to Indians setting fire to vegetation in aboriginal times, and these references cover all major geographic and cultural areas. Fires once started were allowed to burn unchecked...No mention was made of putting out fires or of not starting them in order to protect forest growth." (Steward, 1951).

This appears to be true for the entire New World. Denevan (1992) points out that

"The myth persists that in 1492 the Americas were a sparsely populated wilderness, 'a world of barely perceptible human disturbance.' There is substantial evidence, however, that the Native American landscape of the early sixteenth century was a humanized landscape almost everywhere. Populations were large. Forest composition had been modified, grasslands had been created, wildlife disrupted, and erosion was severe in places. Earthworks, roads, fields, and settlements were ubiquitous. With Indian depopulation in the wake of Old World disease, the environment recovered in many areas. A good argument can be made that the human presence was less visible in 1750 than it was in 1492."

Scholarly review of the use of fire in land management notes that Africa has been called the "*dark continent*" [literal translation is fire-blackened land] ever since the time of Hanna the Carthagian (600 B.C.). Subsequent explorers over the millennia, marvelled at the extensive evidence of fire use by Africans (Kayll, 1974).

Review of the scholarly literature likewise shows that prehistoric man thoroughly altered the European landscape through the agency of fire (Krug and Frink, 1983).

For Polynesia, Trotter and McCulloch (1984) pointed out that

"[B]y the time the first Europeans arrived in New Zealand, [moas] had become extinct...Thirty-four species of birds that were living here when the Polynesians first arrived about a thousand years ago were extinct by the time of the first European contact some eight hundred years later...Populations of marine mammals, shellfish, crustaceans, and a terrestrial reptile were seriously depleted. Vast areas of New Zealand forest had been burned as well. Virtually the entire eastern side of the South Island, and even parts of the high-rainfall western side, were fired, as were eastern, central and northern regions of the North island."

The above shows that pre-industrial human societies used fire to modify the landscape far beyond the areal extent of human habitation. This pattern of pre-industrial landscape modification by man was universal.

For example, Madagascar (the world's fourth largest island) was settled about the time that New Zealand was, 1,000 years ago. Even though Madagascar is ecologically diverse -- ranging from mountainous jungle to semi-arid savannah -- the effect of pre-European, pre-industrial settlement was profound. Dewar (1984) noted

"almost 90 percent of Madagascar had suffered from replacement of the indigenous vegetation by a degraded secondary vegetation...the areas degraded by humans were far larger than the actual areas of habitation and economic activity."

Even the primitive and so-called pristine stone age jewel of the earth -- Papua New Guinea -- has long been a man-made artifact despite the popular perception otherwise: for example as illustrated from the following which appeared on the table of contents of the February 1994 issue of *National Geographic* in regard to its article on Papua New Guinea

"A daughter of U.S. missionaries revisits her childhood home in Papua New Guinea, where logging may soon destroy pristine rain forest and the way of life of the native Bahinemo people."

Popular perception notwithstanding, Papua New Guinea is not pristine. Prehistoric settlement of Papua New Guinea occurred after recovery from the last Ice Age. And then:

"Soon after the climate became sufficiently stable to allow the main vegetation types to assume and maintain roughly their present distributions, there began changes in the balance of the component taxa, indicative of structural changes. They started about 4500 years ago...and continued to the present day. There is little doubt that they were induced by human activity..." (Walker and Flenley, 1979).

And:

"Superimposed on this general degradation of the forest was a second, less dramatic clearing...More generalized degradation of the forest from 4500 I.A. [years ago] onward did not necessitate settled residence so much as avid exploitation by hunting and gathering parties." (Walker and Flenley, 1979).

As with Madagascar, "the areas degraded by humans were far larger than the actual areas of habitation..." (Dewar, 1984).

Because Stone Age Papua New Guinea is not pristine leads to the question -
- How primitive must human beings be in order not to have drastically altered their environs by using fire? The answer lies in Tasmania -- the Australian island State. Tasmanian aborigines were even more primitive than what we moderns call "cave men." Unlike super-primitive "cave men," these aborigines never learned to tie a rock to the end of a stick to make a club. Unlike "cave men," they never learned to tie a sharp rock to the end of a pole to make a spear (e.g., Mulvaney, 1966). When these most primitive people on earth settled Tasmania, temperate rain forests were expanding as the world was recovering from the Ice Age. The most primitive people on earth not only reversed this forest expansion, they also changed the composition of the remaining forests (MacPhail, 1979; 1984).

To quote the review of the subject in *Nature*:

"A marked increase in fire frequency at about 7200 B.P. [years ago] is associated with Aboriginal activity in the area [Tasmania] and this produced a distinct shift in woodland composition in which the rainforest species...which had been previously been expanding, were set into decline. The involvement of fire and of man in the persistence of the wet sclerophyll forest is thus confirmed."

(Moore, 1984).

In conclusion, the above literature is cited as supporting the author's categorizing fire as a natural S emission rather than an industrial one.

B.5.3 Terrestrial Biomass

Recent estimates of S gas emissions from terrestrial biomass are small compared to other natural emission sources, being in the 0.5 Tg S/yr (e.g., Bates et al., 1992) to 0.9 Tg S/yr range (e.g., Spiro et al., 1992).

Anthropogenic S deposition undoubtedly enhances the flux of S emissions from terrestrial biomass. However, this assessment does not consider such anthropogenically-enhanced emissions to be important on the global scale for two reasons. First, total terrestrial biomass S emissions are not significant relative to other natural S emissions. Second, S fertilization appears to have the potential to only fractionally enhance such S emissions because S is a macronutrient whose abundance is in excess relative to ecosystem biological activity (Krug, 1991). Indeed, even for the minority of watersheds which are most S-poor, NAPAP research shows that anthropogenic S deposition accounts for only about 50% of the watershed S budget (Krug, 1991).

B.6 CONCLUSION

Current total estimates of natural sulfur emissions to the atmosphere are between 95.5 and approximately 2500 Tg S/yr. The most likely value is greater than 830 Tg S/yr, which is approximately an order of magnitude greater than the estimated anthropogenic emissions, with approximately 800 Tg associated with sea salt.

Sea salt is by far the largest natural S emission to the atmosphere.

Wind-blown soil (aeolian activity) is an appreciable natural S source to the atmosphere. However, the flux of aeolian S is principally limited to certain arid and semi-arid regions, particularly interior Asia and Australia, where erodible gypsumiferous soils are common.

Estimates of annual flux of S emissions from biomass burning (i.e., fire) are ≥ 2 Tg S/yr. Fire, including the human use of fire, is considered here to be a natural source of S emission rather than an industrial one. Literature is presented to show that aboriginal man has thoroughly shaped the world's terrestrial ecosystems for millennia through the use of fire. History shows that preindustrial societies made extensive use of fire in manipulating their environment, whereas a major thrust of industrial/scientific societies is the development of social and technological instruments to replace destructive wildfires as a means of manipulating the environment for our benefit, i.e., to enhance our ability to provide for our material needs.

Estimates of S gas emissions from terrestrial biomass show such emissions to be small compared to other natural emission sources (Table B.2). Anthropogenic S deposition undoubtedly enhances terrestrial S emission however, on the global scale, this effect appears to be insignificant.

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Table B.1. Estimated world N fertilizer stimulation of marine primary productivity and emissions of S gases assuming Mississippi/Gulf system is globally representative*.

Year	World N Fert. Consumption (10^6 metric tons/yr)	Est. Algal C	Est. S Emission (10^3 metric tons/yr)
1959/60	9.54	3.58	1 - 3
1960/61	10.48	3.94	1 - 3
1961/62	11.59	4.35	1 - 4
1962/63	13.14	4.94	1 - 4
1963/64	14.76	5.55	2 - 5
1964/65	16.47	6.19	2 - 5
1965/66	19.10	7.18	2 - 6
1966/67	22.18	8.33	2 - 7
1967/68	24.21	9.10	3 - 8
1968/69	26.25	9.86	3 - 8
1969/70	28.47	10.70	3 - 9
1970/71	31.76	11.93	4 - 10
1971/72	33.53	12.60	4 - 10
1972/73	36.14	13.58	4 - 11
1973/74	39.20	14.73	4 - 12
1974/75	38.43	14.44	4 - 12
1975/76	44.42	16.69	5 - 14
1976/77	45.26	17.01	5 - 14
1977/78	49.12	18.46	5 - 15
1978/79	54.25	20.38	6 - 17
1979/80	57.22	21.50	6 - 18
1980/81	60.78	22.84	7 - 19
1981/82	60.45	22.71	7 - 19
1982/83	61.19	22.99	7 - 19
1983/84	67.66	25.42	7 - 21
1984/85	70.65	26.55	8 - 22
1985/86	69.83	26.24	8 - 22
1986/87	71.49	26.86	8 - 22
1987/88	75.60	28.41	8 - 24
1988/89	79.61	29.91	9 - 25
1989/90	79.19	29.76	9 - 25
1990/91	77.24	29.02	9 - 24
1991/92	75.46	28.35	8 - 24
1992/93	73.63	27.67	8 - 23

* World Nitrogen Fertilizer Consumption Data: 1960 - 1993 (Harris, 1995).

Table B.2. Estimated Flux of Natural Sulfur Emissions to the Atmosphere.

Source	Range (Tg S/yr)		Best Estimate
Sea Salt	80	- 2,400	≥ 800
Marine Gases	11.9	- 54	≥ 11.9
Vulcanism	0.75	- 42	≥ 9
Aeolian	0.35	- 10	≥ 6.7
Fire	2.0	- 2.3	≥ 2.0
Terrestrial Biomass	0.5	- 0.9	≥ 0.5
TOTAL	95.5	- ~2,500	≥ 830.1

Table B.3. Estimated world anthropogenic N emission stimulation of marine primary productivity and marine S gas emissions from 1860 to 1990*.

Year	Est. World N Emission (10 ⁶ metric tons)	Est. Algal C	Est. S Emission (10 ³ metric tons)
1860	0.4	2.0	1 - 2
1870	0.7	3.4	1 - 3
1880	0.9	4.4	1 - 4
1890	1.3	6.4	2 - 5
1900	2.2	11	3 - 9
1910	3.3	16	5 - 13
1920	4.2	21	6 - 17
1930	4.9	24	7 - 20
1940	5.7	28	8 - 23
1950	6.8	33	10 - 28
1960	11.8	57.8	17 - 48
1970	17.6	86.2	25 - 72
1980	22.1	108	32 - 90
1990**	23.9	117	34 - 98

* 1860 to 1980 estimated world N emission data from Dignon and Hameed (1989).

** 1990 estimated world N emission data from Table B.4.

Table B.4. Anthropogenic nitrogen emissions: 1990*.

Region/ Country	Total N Emissions (103 metric tons/yr)	Region/ Country	Total N Emissions (103 metric tons/yr)
<u>NORTH AMERICA</u>	<u>6610</u>	Germany, Dem. Rep.	214
Canada	591	Germany, Fed. Rep.	823
United States	6019	Greece	227
<u>ASIA</u>	<u>5094</u>	Hungary	72
Afghanistan	9	Iceland	4
Bangladesh	20	Ireland	41
Brunei	3	Italy	534
Cambodia	4	Luxembourg	5
China	2240	Netherlands	161
China, Taiwan	99	Norway	64
Hong Kong	30	Poland	389
India	778	Portugal	43
Indonesia	194	Romania	119
Israel	45	Spain	289
Japan	590	Sweden	113
Korea	169	Switzerland	56
Korea, Dem.	142	UK	817
Laos	3	Yugoslavia	128
Macao	2	<u>USSR</u>	<u>2046</u>
Malaysia	54	Armenia	7
Maldives	0	Azerbaijan	18
Mongolia	22	Belarus	31
Myanmar	14	Estonia	6
Nepal	15	Georgia	7
Pakistan	70	Kazakhstan	100
Philippines	56	Kyrgystan	4
Qatar	16	Latvia	4
Saudi Arabia (1985)	236	Lithuania	11
Singapore	27	Moldava	12
Sri Lanka	11	Russia	927
Thailand	117	Tajikistan	2
Turkey	53	Turkmenistan	11
United Arab Em. (1985)	45	Ukraine	231
Vietnam	30	Uzbekistan	36
<u>EUROPE</u>	<u>5338</u>	<u>SOUTH AMERICA**</u>	<u>2340</u>
Albania (1985)	3	<u>AFRICA**</u>	<u>1860</u>
Austria	63	<u>OCEANIA**</u>	<u>620</u>
Belgium	91		
Bulgaria	46		
Czechoslovakia	341		
Denmark	77		
Finland	88		
France	530		
		TOTAL =	23,908.

* Data from United Nations Environment Programme (1993).

** 1980 data from Dignon and Hameed (1989).

Table B.5. Discharge of sediment from the Mississippi River into the Gulf of Mexico: 1851 - 1982*.

Time	Sediment (10^6 metric tons/yr)
1851 - 1893	681**
1930 - 1952	463
1953 - 1962	214
1963 - 1982	141

* Data from Kesel (1988), Mississippi sediment load at Tarbert.

** Sediment data from New Orleans. Much of the Mississippi's discharge to the Gulf of Mexico bypasses New Orleans. Therefore New Orleans 1851- 1893 sediment load was weighted by 1.72, the arithmetic average ratio of Tarbert/New Orleans sediment loads for the measured time periods.

Table B.6. Variation in southern ocean DMS emissions inferred from MSA in a South Pole ice core*.

Year	Quantity in Peak (X Background)	Estimated Range (Tg S/yr)
Est. Background	1	6.5 - 8.8
1983	10	65 - 88
1982	10	65 - 88
1976	3.7	24 - 33
1975	3.2	21 - 28
1972	6.2	40 - 55
1965	1.5	9.7 - 13
1963**	1.4	9.1 - 12
1958	4.3	28 - 38
1957	4.3	28 - 38
1945**	1.5	9.8 - 13
1941	3.5	23 - 31
1933**	2.5	16 - 22
1928**	5.0	33 - 44

* Ice core data from Legrand and Feniet-Saigne (1991). Range in background marine DMS emissions are developed from Bates *et al.* (1992) and Spiro *et al.* (1992). See text for more explanation.

** Quantity of MSA deviates from peak intensity. Peak intensity divided by 2 to reflect approximate half-year duration of the peak.

APPENDIX C

Sulfur Emissions from Volcanic Activity in 1985 and 1990

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C.1. INTRODUCTION

Sulfur from anthropogenic sources is emitted in the form of sulfur dioxide (SO_2), hydrogen sulfide (H_2S), or sulfate; estimates of the sulfate fraction vary from 1.5 to 5% (Benkovitz et al., 1994). Global estimates of anthropogenic emissions of sulfur for 1985 are approximately 65 Tg S y^{-1} (Benkovitz et al., 1996) and for 1990 approximately 71 Tg S y^{-1} (see Appendix A titled Global Anthropogenic Sulfur Emissions for 1985 and 1990 in this report). Sulfur from biogenic sources is emitted in the form of SO_2 and of several reduced sulfur compounds such as hydrogen sulfide (H_2S), dimethyl sulfide (DMS), carbonyl sulfide (OCS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS). Recent estimates of emissions of sulfur compounds from non-anthropogenic sources (Bates et al., 1992) place oceanic emissions (mostly DMS) at approximately 15 Tg S y^{-1} , terrestrial emissions at approximately 0.4 Tg S y^{-1} , emissions from biomass burning at approximately 2 Tg S y^{-1} and volcanic emissions at approximately 9 Tg S y^{-1} , for a total of 26.4 Tg S y^{-1} . These estimates for oceanic and terrestrial sulfur emissions are at the low end of the range given by the IPCC (Houghton et al., 1992), where oceanic emissions are estimated to be in the range 10 to 50 Tg S y^{-1} and terrestrial emissions in the range 0.2 to 4 Tg S y^{-1} .

Sulfur emissions from anthropogenic sources are strongly localized in the highly populated and industrialized regions in Eastern North America, and across Europe from the United Kingdom over Central Europe to the Donbas region

in Russia (Benkovitz et al., 1996). Release heights are in the range of surface to over 200 m (Saeger et al., 1989). Biogenic sulfur emissions from oceanic sources follow the distribution of areas of high productivity which are dependent on season and are located preferentially along coastlines. Sulfur emissions from land sources follow the distribution of global vegetation and are highest in the tropical and subtropical areas. All the biogenic emissions are released at the surface (Benkovitz et al., 1994). Volcanic emissions are located in areas of volcanic activity, are extremely variable in time, and can be released anywhere from ground level to the stratosphere.

The main sulfur compound emitted by volcanoes is sulfur SO_2 (Gerlach and Nordie, 1975). Hydrogen sulfide (H_2S) may be abundant in plumes of relatively low temperatures and reducing conditions (Ozawa, 1966, Ross, 1968); however, overall this compound is generally less than 1% of the sulfur gas (Stoiber et al., 1987). Other sulfur compounds present in small amounts are sulfur trioxide (SO_3), sulfate, carbonyl sulfide (OCS), and elemental sulfur (S). For example, Belviso et al. (1986) estimate the global OCS volcanic yield to be 3.1 to $46.1 \times 10^9 \text{ g S yr}^{-1}$, compared to an annual flux of $3.4 \times 10^{12} \text{ g S yr}^{-1}$ for SO_2 estimated by Stoiber et al (1987). Reduced sulfur compounds can be oxidized as the hot eruption mixes with ambient oxygen, so that the composition of sulfur gases in volcanic activity can vary widely (Cadle et al., 1971).

Sulfur emission rates of volcanoes have recently begun to be estimated based on surface measurements (e.g., Stoiber et al., 1983; Allard et al., 1994, Caltabiano et al., 1994) and derived from satellite measurements (Bluth et al., 1993, Mouginis-Mark et al., 1989). Lacking direct measurements,

various methodologies to estimate sulfur emissions have been developed and applied to obtain estimates of the contribution of volcanoes to the global atmospheric sulfur budget; for example, see Newhall and Self (1982), Berresheim and Jaeschke (1983), Devine *et al.* (1984b), Stoiber *et al.*, (1987), and Pinto *et al.* (1989). Several of these methodologies and estimates have been included as a component of global inventories of sulfur emissions from all sources by various authors; for example, see Cullis and Hirschler (1980), Möller (1984), Bates *et al.* (1992), and Spiro *et al.* (1992). In general, global estimates of total sulfur emissions are given as global totals for an "average" year, except in the Spiro *et al.* inventory, where the data reflect the year 1980.

Much more attention has been given to sulfur emissions from erupting volcanos since these were considered a more abundant source of sulfur compounds; for example, Stoiber *et al.* (1987) estimate that the annual sulfur flux from degassing, non-erupting volcanoes is approximately 53% of the flux from eruptive events. For their estimate, these authors used average, normalized data for the previous 20 years based on the compendium of Simkin *et al.* (1981). In contrast, Bluth *et al.* (1993) used data from the Total Ozone Mapping Spectrometer aboard NIMBUS 7 to estimate that from November 1978 to May 1993 the annual flux from explosive volcanism is less than half of the non-explosive output. These results give an indication of the interannual variability of the volcano sulfur source, so that applying averages to obtain emissions estimates would not yield the correct picture of these emissions for particular years.

The purpose of this project is to compile estimates of sulfur emissions from volcanic activity for years 1985 and 1990.

C.2. EMISSIONS OF SULFUR FROM VOLCANOES FOR 1985 AND 1990.

C.2.1. Estimation of sulfur emissions from volcanoes.

Petrologic estimates and direct measurements are the two prevalent methodologies used to estimate sulfur emissions from volcanoes. In addition the algorithms used to estimate various parameters of large eruption plumes from satellite measurements have been developed and are being refined.

The petrologic method assumes that the volatile contents of melt inclusions trapped in crystals represent those of the pre-eruption melt, and that the volatile contents of coexisting degassed matrix glass represent those of the melt after eruption (Gerlach *et al.*, 1994); the difference is taken as a measure of volatile degassing which, scaled up to the mass of erupted melt, yields estimates of volcanic emissions of SO_2 and other volatiles (Cl, F) during eruptions (Devine *et al.*, 1984a, Johnson, 1980, Palais and Sigurdsson, 1989, Sigurdsson, 1990, Sigurdsson *et al.*, 1985). Petrologic estimates of volatile emissions during eruptions are taken to be minimum estimates, since the assumptions inherent in the method may not be fully satisfied and lead to low results (Devine *et al.*, 1984a, Palais and Sigurdsson, 1989).

Direct measurement techniques using the correlation spectrometer (COSPEC) have been used since 1973 and the satellite-based Total Ozone Mapping Spectrometer (TOMS) has been used since 1978 to measure SO_2 emissions by remote sensing during volcanic eruptions (Gerlach *et al.*, 1994). The correlation spectrometer method uses the solar ultraviolet light transmitted and scattered by the earth's atmosphere as an illumination source. With the instrument directed towards the sky, the COSPEC measures the amount of ultraviolet light absorbed by SO_2 molecules present along the optical path in units of concentration-path length (ppm-m). Calibration is performed by using

a pair of internal standards with known concentrations of SO_2 . A profile of SO_2 concentration across the plume is measured at a right angle to the axis of the plume. The product of the concentration-path length (ppm-m), the width of the plume (m), and the plume speed (m/s) gives the emission rate of SO_2 which is reported in metric tons (10^3 kg) per day (t/d).

In addition to actual variation in the discharge rate, measured SO_2 emission rates may vary due to fluctuations in the wind speed and direction, change in conditions of cloud cover, change of sun angle and amount of solar ultraviolet radiation, and variation in plume opacity due to suspended ash particles. Uncertainty in COSPEC measurements arises from several operational factors including instrument calibration ($\pm 2\%$) and chart reading error ($\pm 4\%$), variation in aircraft speed during the measurement traverse ($\pm 5\%$), operator variance affecting instrument operation and reduction of the data ($\pm 5\%$), and measurement of wind speed and direction ($\pm 10\text{-}40\%$) (Casadevall et al., 1981, Stoiber et al., 1983).

C.2.2. Development of Sulfur Emission Estimates for 1985 and 1990

The basic information on volcanoes was taken from the computerized data file of Simkin and Siebert (1994). This information includes the location and summit height of the volcano, activity, 'continuity' or 'discontinuity' of the eruptions, and the Volcanic Explosive Index (VEI). The monthly bulletins of the Scientific Event Alert Network (SEAN) which report seismic and volcanic activity and other such events were used as the primary source of information for the years of interest. Detailed information on volcanic activity such as height of the ash/gas column, SO_2 emission rates, start and stop date and emission type, were taken from the SEAN bulletins and

from the literature, for example, Caltabiano (1994), Casadevall (1994), Andres (1991), and Allard (1994). If available, minimum, average and maximum emission estimates were recorded. Ash/gas columns, lava flow, and other activity were reported from some volcanoes which were not listed to be active for the years 1985 and 1990 by Simkin and Siebert (1994); we have classified these cases as non-eruptive, degassing activities.

The TOMS estimates of the sulfur emissions from major volcanic activity in 1985 and 1990 were received from G. Bluth (personal communication, 1994). These data have been discussed in Bluth *et al.* (1993), Krueger *et al.* (1990), Shannon and Bluth (1994), and Schnetzler *et al.* (1994). The algorithms used to retrieve the volcanic emissions information from satellite measurements are currently under review.

Sulfur emissions were estimated for all volcanic activity in both years using the methodology of Stoiber *et al.* (1987) which bases the estimates on the type of eruption (continuous or episodic), the volcano location (at a convergent plate margin or other) and the VEI. We assumed that all volcanoes listed as active in the two years of interest are located at convergent plate margins. This assumption is based on the fact that only 5% of all volcanoes listed by Simkin and Siebert (1994) are of the divergent margin type (rift volcanism). Moreover, the 'spreading apart' of major plates is characterized by the relatively nonexplosive outpouring of fluid lava and *commonly* takes place one or more kilometers below the surface of the ocean (Simkin and Siebert, 1994). In addition, such volcanism is dominant in regions like East Africa and Iceland, where the spreading apart of the plates takes place above sea level (Simkin and Siebert, 1994). None of the volcanoes located in East Africa or Iceland are shown to be active for the years 1985 or 1990 in the

sources consulted.

C.3.3. Initial Results

Table C.3.3.1 presents information on the volcanoes that were active in 1985 and the sulfur emissions that have been estimated. Table C.3.3.2 presents the same information for volcanoes active in 1990. Columns labeled 'Literature' present emissions estimates obtained from the SEAN bulletins and/or the literature (column labeled 'Mid'), with estimated ranges if available (columns labeled 'Low' and 'High'). Column labeled 'Simkin/Stoiber' presents the emissions estimates obtained by using the data from Simkin and Siebert (1994) and the methodology of Stoiber et al. (1987). Stoiber's methodology consistently overestimates sulfur emissions, often by an order of magnitude or more, when compared to the literature values which are volcano-specific and generally based on some measurement data. In addition to the inherent uncertainty in the correlation between the VEI and the sulfur emissions, there is also some uncertainty in the 'continuity/discontinuity' classification for the eruptions of some volcanoes. These uncertainties are significant for volcanoes of higher VEI. For example with a VEI of 3, a *non-continuous eruption* as per Stoiber would have 2.87 Tg yr^{-1} total sulfur flux as against 0.075 Tg yr^{-1} for a *continuous eruption*. Therefore we consider estimates based on the Stoiber methodology to be an upper value for sulfur emissions.

The columns labeled 'Current Estimate' present what we consider to be best estimates from the data sources accessed. These estimates are a combination of the literature values when available, defaulting to the Simkin/Stoiber estimate when no other data are available. Our current

estimate of the total sulfur emitted by volcanic activity in 1985 is 29.6 Tg SO₂ from 41 active volcanoes; literature estimates are available for only 12 (29%) of these volcanoes. Emissions based on literature values total 1.4 Tg SO₂; the corresponding Simkin/Stoiber estimates total 10.8 Tg SO₂. Our current estimate of the total sulfur emitted by volcanic activity in 1990 is 23.3 Tg SO₂ from 44 active volcanoes; literature estimates are available for only 15 (34%) of these volcanoes. Emissions based on literature values total 7.2 Tg SO₂; the corresponding Simkin/Stoiber estimates total 12.5 Tg SO₂. The much smaller difference in the totals for 1990 is the result of estimates of the activity of Mt. Etna during this year. Literature estimates, based on monthly COSPEC measurements of the plume, are higher (by a factor of 3) than the Simkin/Stoiber estimates, compensating for the greater difference between the estimates for the other volcanoes. The major difference in volcanic activity between the two years is provided by the eruptions of Mt. Etna and Redoubt; Mt. Etna showed only non-eruptive activity in 1985 and Redoubt showed no activity for this year. These results, although preliminary, provide graphic illustration of the variability of the volcanic source of sulfur emissions.

Work on this project continues. The on-going literature search is expected to provide volcano-specific estimates of the sulfur emissions from additional volcanoes active in these two years. Other data sources being consulted include the Smithsonian Institution Global Volcanism Program and World Data center A for Solid Physics in Boulder, CO.

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List of Acronyms in Appendix C

COSPEC: COrelation SPECTrometer.
IPCC: Intergovernmental Panel on Climate Change.
SEAN: Scientific Event Alert Network.
TOMS: Total Ozone Mapping Spectrometer.
VEI: Volcanic Explosivity Index.

Table C.3.3.1 Estimate of Sulfur Emissions from Volcanic Activity in 1985

Volcano Name	Region	Sub region	Latitude	Longitude	Estimated Sulfur Emissions (Tg SO ₂)				
					Literature Low	Mid	High	Simkin/ Stoiber	Current Estimate
ETNA	Europe	Italy	37.73 N	15.00 E				1.640	1.640
STROMBOLI		Italy	38.79 N	15.21 E	0.201	0.243	0.285	2.090	0.243
FOURNAISE, PITON DE	AustralAsia	Indian O.-W	21.23 S	55.71 E				0.329	0.329
HEARD		Indian O.-S	53.11 S	73.51 E		0.010		2.090	0.010
RUAPEHU		New Zealand	39.28 S	175.57 E				0.329	0.329
NIUAFO'OU	Pacific	Tonga-SW Pacific	15.60 S	175.63 W				0.020	0.020
MANAM		New Guinea	4.10 S	145.06 E				1.640	1.640
LANGILA		New Britain	5.53 S	148.42 E				0.075	0.075
ULAWUN		New Britain	5.05 S	151.33 E		0.075		0.329	0.075
BAGANA		Bougainville	6.14 S	155.20 E				0.329	0.329
KAVACHI		Solomon Islands	9.02 S	157.95 E				0.170	0.170
PAGAN, MT.		Mariana Is land	18.13 N	145.80 E				1.640	1.640
TINAKULA		Santa Cruz Island	10.38 S	165.80 E				1.640	1.640
TANGKUBANPARAHU	South East & Far East Asia	Java	6.77 S	107.60 E				0.170	0.170
SEMERU		Java	8.11 S	112.92 E				1.640	1.640
RAUNG		Java	8.13 S	114.04 E				2.090	2.090
SANGEANG API		Lesser Sunda Is	8.18 S	119.06 E				2.870	2.870
SOPUTAN		Sulawesi-Indonesia	1.11 N	124.73 E				2.090	2.090
API SIAU		Sangihe Is-Indones	2.78 N	125.48 E				1.640	1.640
CANLAON		Philippines-C	10.41 N	123.13 E		0.010		0.170	0.010
SUWANOSE-JIMA		Ryukyu Is	29.53 N	129.72 E				1.640	1.640
SAKURA-JIMA		Kyushu-Japan	31.58 N	130.67 E		0.262		1.640	0.262
ASO		Kyushu-Japan	32.88 N	131.10 E		0.016		0.329	0.016
FUKUTOKU-OKA-NO-BA		Bonin Is-Japan	24.28 N	141.52 E				0.084	0.084
TOKACHI		Hokkaido-Japan	43.42 N	142.68 E				0.170	0.170
GORELY		Kamchatka	52.56 N	158.03 E				1.640	1.640
BEZYMIANNY		Kamchatka	55.97 N	160.60 E		0.010		0.075	0.010
KLIUCHEVSKOI		Kamchatka	56.06 N	160.64 E		0.010		1.640	0.010

Table C.3.3.1 Estimate of Sulfur Emissions from Volcanic Activity in 1985

Volcano Name	Region	Sub region	Latitude	Longitude	Estimated Sulfur Emissions (Tg SO ₂)				
					Literature			Simkin/ Stoiber	Current Estimate
					Low	Mid	High		
CLEVELAND		Aleutian Is	52.81 N	169.95 W				0.005	0.005
ST. HELENS, MT. (3)	America	US-Washington	46.20 N	122.18 W	0.014	0.016	0.019	0.170	0.016
KILAUEA		Hawaiian Is	19.43 N	155.29 W				0.329	0.329
LOIHI SEAMONT		Hawaii	18.92 N	155.25 W				0.020	0.020
PACAYA		Guatemala	14.38 N	90.60 W				0.329	0.329
SAN CRISTOBAL		Nicaragua	12.70 N	87.00 W				0.005	0.005
MASAYA		Nicaragua	11.98 N	86.16 W				0.329	0.329
CONCEPCION (4)		Nicaragua	11.54 N	85.62 W			0.010	0.329	0.010
ARENAL		Costa Rica	10.46 N	84.70 W				1.640	1.640
RUIZ (4)		Colombia	4.90 N	75.32 W			0.750	1.640	0.750
VILLARRICA		Chile-C	39.42 S	71.95 W				1.640	1.640
BEERENBERG JAN MAYEN		Atl-N-Jan Mayen	71.08 N	8.17 W				2.090	2.090
EREBUS, MT. (3)	Antarctica	Antarctica	77.53 S	167.17 E			0.011	0.329	0.011
Totals						1.423		39.054	29.646

Table C.3.3.1 Estimate of Sulfur Emissions from Volcanic Activity in 1985

References

Simkin/Stoiber (Simkin and Siebert, 1994; Stoiber *et al.*, 1987).

(1) (Allard *et al.*, 1994).

(2) (Caltabiano *et al.*, 1994).

(3) SEAN bulletin.

(4) TOMS data.

(5) (Ohta 1988).

(6) (Hirabayashi *et al.*, 1995).

Table C.3.3.2 Estimate of Sulfur Emissions from Volcanic Activity in 1990

Volcano Name		Region	Sub region	Latitude	Longitude	Estimated Sulfur Emissions (Tg SO ₂)				
						Low	Literature Mid	High	Sinkin/ Stoiber	Current Estimate
STROMBOLI	(1)	Europe	Italy	38.79 N	15.21 E	0.428	0.445	0.461	0.329	0.445
ETNA	(2)		Italy	37.73 N	15.00 E		2.659		0.329	2.658
AKUTAN			Aleutian Is	54.13 N	165.97 W				0.170	0.17
FOURNAISE, PITON DE		AustraliaAsia	Indian O.-W	21.23 S	55.71 E				0.084	0.084
WHITE ISLAND			New Zealand	37.52 S	177.18 E				0.170	0.17
RUAPEHU			New Zealand	39.28 S	175.57 E				0.329	0.329
MANAM		Pacific	New Guinea-NE of	4.10 S	145.06 E				1.640	1.64
LANGILA			New Britain-SW Pac	5.53 S	148.42 E				1.640	1.64
ULAWUN			New Britain-SW Pac	5.05 S	151.33 E				0.005	0.005
RABAU CALDERA			New Britain-SW Pac	4.27 S	152.20 E				0.005	0.005
BAGANA			Bougainville-S W Pac	6.14 S	155.20 E				0.329	0.329
YASUR	(3)		Vanuatu-SW Pacific	19.52 S	169.43 E	0.219	0.438	0.657	0.158	0.438
PAGAN, MT.			Mariana Is-C Pac	18.13 N	145.80 E				[1]	
AGRIGAN			Mariana Is-C Pac	18.77 N	145.67 E				0.005	0.005
MERAPI		South East and Java		7.54 S	110.44 E				0.329	0.329

Table C.3.3.2 Estimate of Sulfur Emissions from Volcanic Activity in 1990

Volcano Name		Region	Sub region	Latitude	Longitude	Estimated Sulfur Emissions (Tg SO ₂)				
						Low	Literature Mid	High	Simkin/ Stoiber	Current Estimate
KELUT	(4)	Far East Asia	Java	7.93 S	112.31 E	0.150	0.150	0.150	0.910	0.15
RAUNG			Java	8.13 S	114.04 E				1.640	1.64
GAMALAMA			Halmahera-Indonesia	0.80 N	127.33 E				0.075	0.075
SAKURA-JIMA	(5)		Kyushu-Japan	31.58 N	130.67 E		0.660		1.640	0.66
UNZEN	(6)		Kyushu-Japan	32.75 N	130.30 E		0.008		0.170	0.008
ASO	(5)		Kyushu-Japan	32.88 N	131.10 E		0.016		0.020	0.016
ASAMA	(5)		Honshu-Japan	36.40 N	138.53 E		0.037		2.090	0.036
OSHIMA			Izu Is-Japan	34.73 N	139.38 E				2.090	2.09
KLIUCHEVSKOI			Kamchatka	56.06 N	160.64 E				0.075	0.075
REDOUBT	(3)	America	Alaska-SW	60.48 N	152.75 W		1.127		2.870	1.127
ST. HELENS, MT.			US-Washington	46.20 N	122.18 W				1.640	1.64
KILAUEA			Hawaiian Is	19.43 N	155.29 W				0.084	0.084
COLIMA VOLC COMPLEX			Mexico	19.51 N	103.62 W				0.084	0.084
SANTIAGUITO DOME	(3)		Guatemala	14.76 N	91.55 W	0.012	0.018	0.023	0.075	0.018
FUEGO	(3)		Guatemala	14.47 N	90.88 W	0.059	0.070	0.082	[1]	0.07
PACAYA	(3)		Guatemala	14.38 N	90.60 W		0.011		1.640	0.011
ARENAL			Costa Rica	10.46 N	84.70 W				1.640	1.64

Table C.3.3.2 Estimate of Sulfur Emissions from Volcanic Activity in 1990

Volcano Name	Region	Sub region	Latitude	Longitude	Estimated Sulfur Emissions (Tg SO ₂)				
					Literature			Simkin/ Stoiber	Current Estimate
				Low	Mid	High			
POAS		Costa Rica	10.20 N	84.23 W			0.329	0.329	
RUIZ	(3)	Colombia	4.90 N	75.32 W		0.699	1.640	0.699	
GALERAS	(3)	Colombia	1.22 N	77.37 W		0.873	0.329	0.873	
REVENTADOR		Ecuador	0.08 S	77.66 W			0.005	0.005	
GUAGUA PICHINCHA		Ecuador	0.17 S	78.60 W			0.170	0.17	
SABANCAYA		Peru	15.78 S	71.85 W			1.640	1.64	
LASCAR		Chile-N	23.37 S	67.73 W			0.093	0.093	
PULAR		Chile-N	24.18 S	68.05 W			0.093	0.093	
LONQUIMAY		Chile-C	38.37 S	71.58 W			1.640	1.64	
LLAIMA		Chile-C	38.70 S	71.70 W			0.093	0.093	
KICK-'EM-JENNY		W Indies	12.30 N	61.63 W			0.020	0.02	
EREBUS, MT.	(3)	Antarctica	77.53 S	167.17 E		0.037	0.329	0.037	
Totals						7.245	28.631	23.348	

Notes

[1] VEI information not given in Simkin and Siebert (1994).

References

Simkin/Stoiber (Simkin and Siebert, 1994, Stoiber et al., 1987).

Table C.3.3.2 Estimate of Sulfur Emissions from Volcanic Activity in 1990

- (1) (Allard *et al.*, 1994).
- (2) (Caltabiano *et al.*, 1994).
- (3) Scientific Event Alert Network (SEAN) bulletin.
- (4) TOMS data.
- (5) (Ohta, 1988).
- (6) (Hirabayashi *et al.*, 1995)