OXIDES OF CARBON

P.A. Siskos and P.P. Georgiou
National Kapodistrian University of Athens, Zografos, Athens, Greece

Keywords: carbon cycle, sources, atmosphere, carbon monoxide, poisoning, combustion, indoor air pollution, health effects, fossil fuels, carbon dioxide, greenhouse effect, deforestation, ozone, photosynthesis, anthropogenic, power plants, capture, storage, scrubbing

Contents

Summary

Carbon forms with oxygen two environmentally important gases: carbon monoxide and carbon dioxide. Carbon oxides are significant components of the atmosphere and they are parts of the carbon cycle. Carbon monoxide is produced whenever organic matter is burnt in a limited quantity of oxygen. For this reason it is found in the exhaust gases of motor vehicles as well as in cigarette smoke. Carbon monoxide is also of global concern as it is an extremely dangerous poison. It can cause suffocation if sufficient amounts are present. Since it is a colorless and tasteless gas it gives no warning of its presence. Currently, the most effective reduction of carbon monoxide emission from automobile engines is the catalytic converter.

Carbon dioxide is naturally produced by respiration and metabolism and consumed by plants during photosynthesis. It is also released in the atmosphere when carbon

containing fossil fuels such as oil, natural gas and coal are burned in air. Since the beginning of Industrial Revolution (1750), increased amount of carbon dioxide has been released in the atmosphere due to industrial activities. Although it is essential for life, carbon dioxide is also the major cause of an additional greenhouse effect. Capture and storage of carbon dioxide from stationary sources has the potential to make deep reductions in greenhouse gas emissions, although it has only recently been seriously considered as a potential method for reducing emissions. There are also many schemes and potential options for the reuse of carbon dioxide captured.

1. Introduction: The Carbon Cycle

Atmospheric scientists, oceanographers, and ecologists have attempted for several decades to develop an accurate global budget of carbon in the Earth system. Although great accomplishments have been made, balancing the carbon budget remains problematic, largely because of the difficulty of measuring carbon fluxes accurately over large scales and of modeling oceanic and atmospheric transport of carbon species.

Atmospheric, oceanic, and terrestrial pools of carbon are extremely large and fluxes between pools are bidirectional and nearly in balance. Despite these difficulties, significant progress has been made. A global carbon budget is illustrated in Figure 1, which presents current best estimates of the amount of carbon held in several important reservoirs and the magnitude of annual fluxes between them, as indicated by the arrows. Figure 1 shows that the total anthropogenic input of carbon dioxide (CO_2) to the atmosphere (7.1 Gt carbon per year) represents a significant perturbation of the natural carbon cycle.

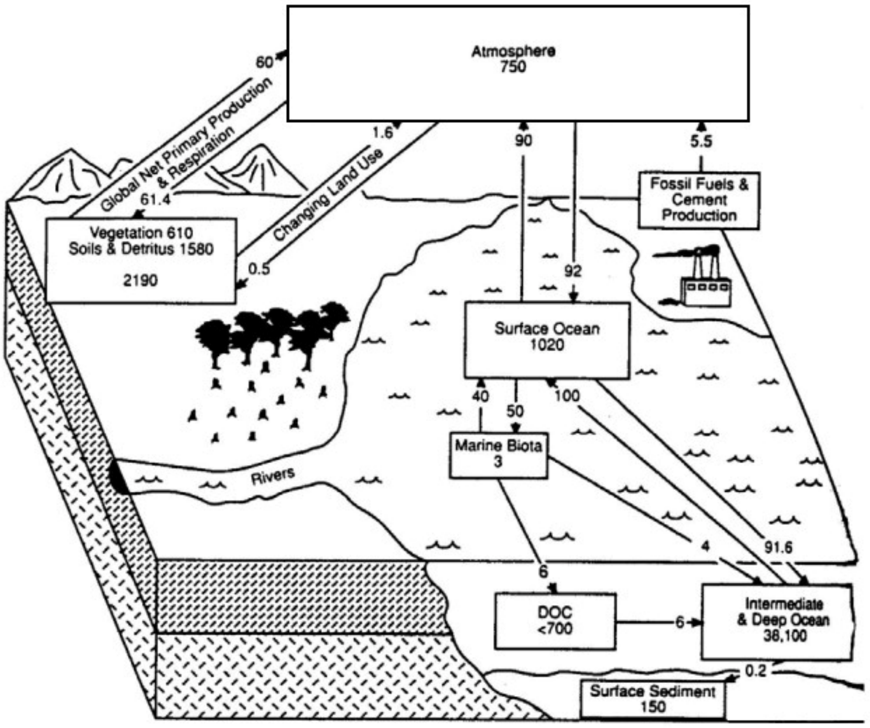

Figure 1: Global carbon cycle showing carbon pools (GtC) and average fluxes (GtC y^{-1})

for the period 1980-1989
IPCC (1996). Houghton J.T., Filho L.G., Callander B.A., Harris A., Kattenberg A., Maskell K., (Eds). *Climate Change 1995: The Science of Climate Change.* Cambridge, UK: Cambridge University Press. Schimel D.S. (1995). Terrestrial ecosystems and the carbon cycle, *Global Change Biology* 1, 77-92.

1.1. Ocean Carbon Processes and Surface Fluxes

Although, on the global scale, the exchanges of CO_2 between the ocean and the atmosphere are nearly equilibrated, large imbalances can occur locally. The net exchange flux at a given location depends on the degree of saturation of CO_2 in the surface waters and it can be expressed by:

$$F_{\text{net}} = K\ (p_{\text{CO}_2\text{-ocean}} - p_{\text{CO}_2\text{-atm}}) \qquad (1)$$

where $p_{\text{CO}_2\text{-atm}}$ represents the partial pressures of CO_2 in the air and $p_{\text{CO}_2\text{-ocean}}$ represents an equilibrium CO_2 partial pressure in the ocean surface waters. K is an exchange coefficient that increases with wind speed (turbulence) at the air-sea interface. $p_{\text{CO}_2\text{-ocean}}$ varies with a variety of factors including temperature and oceanic biological activity.

The dissolution of CO_2 in sea water is achieved through the following reactions:

$$\text{CO}_2\ (\text{g}) \rightarrow \text{CO}_2\ (\text{aq}) \qquad (2)$$

$$\text{CO}_2\ (\text{aq}) + \text{H}_2\text{O} \rightleftarrows \text{H}_2\text{CO}_3 \qquad (3)$$

$$\text{H}_2\text{CO}_3 \rightleftarrows \text{HCO}_3^- + \text{H}^+ \qquad (4)$$

$$\text{HCO}_3^- \rightleftarrows \text{CO}_3^{2-} + \text{H}^+ \qquad (5)$$

where (g) and (aq) stand for gas and aqueous phase respectively. The relative abundance of CO_2 (aq), CO_3^{2-}, and HCO_3^- is determined by the activity of hydrogen ions in water (pH) and the equilibrium constants of the above reactions, which vary with temperature, water salinity, and to a lesser extent, pressure. Figure 2 shows the partitioning of inorganic carbon species as a function of water pH.

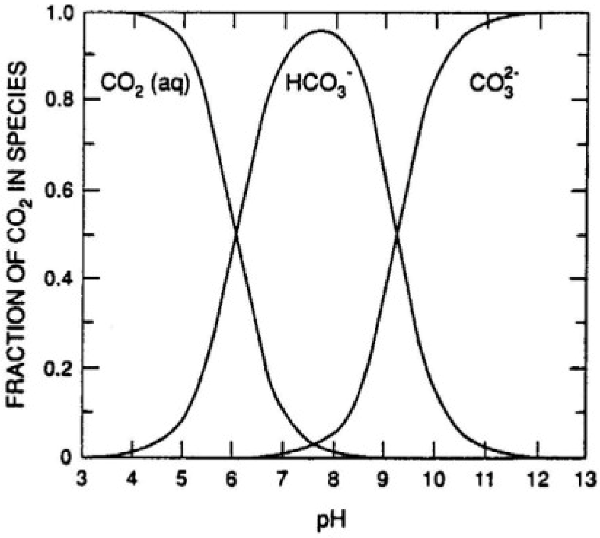

Figure 2. Relative concentration of dissolved carbon species in sea water calculated as a function of pH for a temperature of 15 ºC and a salinity of 35 percent.
Mehrbach C., Culberson C.H., Hawley S.E., Pytkowiez R.M. (1973). Measurement of the apparent dissociation constants of carbonic acid in sea water at atmospheric pressure. *Limnology and Oceanography* 18, 897-.

Since the pH of the ocean is usually close to 8.0, the predominant compound is the bicarbonate ion (HCO_3^-). However, in some fresh water ecosystems the pH of rivers and streams may vary between 3 and 8, with a shifting in the inorganic carbonate ion chemistry.

The transfer of carbon to the depths of the ocean is achieved by sedimentation of calcium carbonate ($CaCO_3$). There is little evidence of inorganic precipitation of $CaCO_3$, except perhaps in warm tropical waters. The predominant formation of $CaCO_3$ is provided by shell-forming organisms (algae, protozoa, corals, etc.) residing in sunlit surface waters. A large fraction of the carbonate sediments is therefore produced in nutrient rich regions, especially in shelf zones where detritus of continental origin is advected by rivers. As these carbonates, as well as the calcareous remains of organisms, settle toward the bottom of the ocean, they dissolve in deep waters, and only a small fraction reaches the ocean floor.

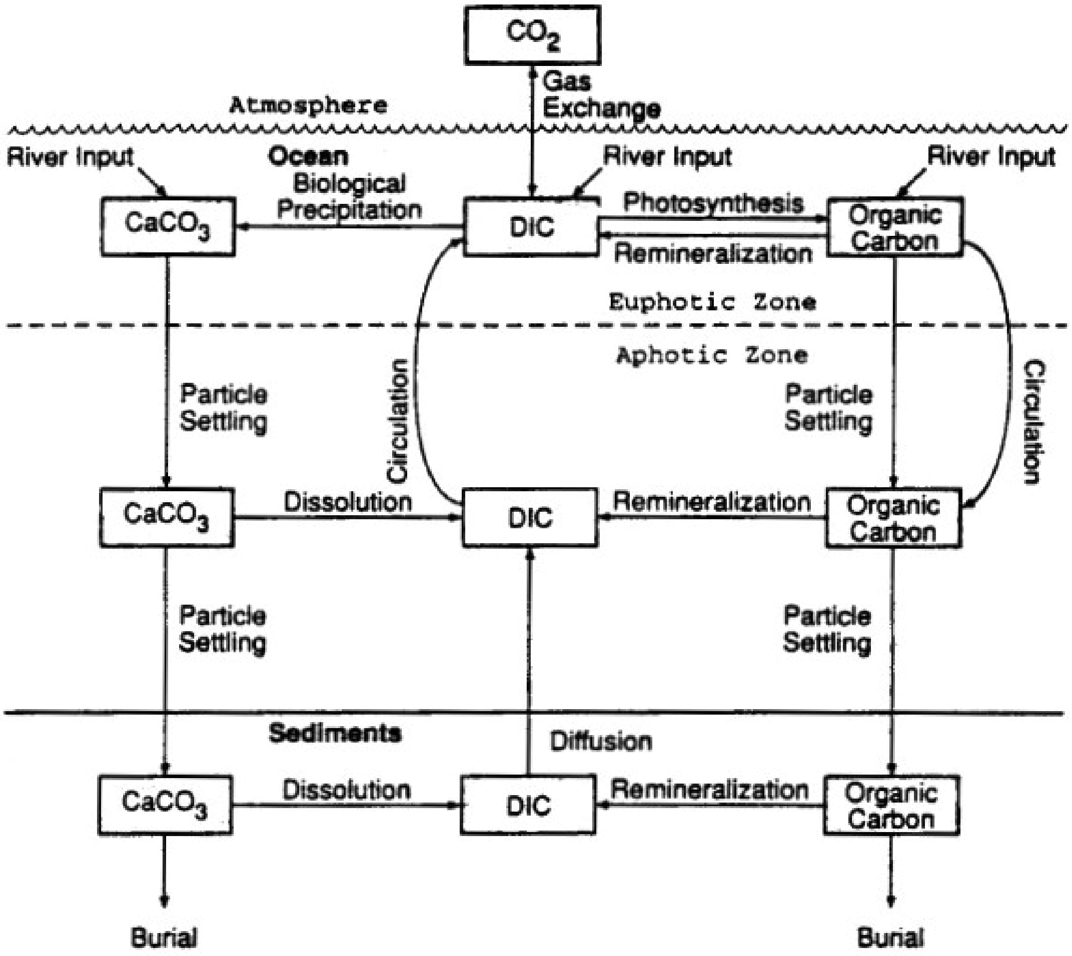

Figure 3. The carbon cycle in the ocean
Najjar R. (1992). Marine biochemistry. In: Climate System Modeling, (ed. K. Trenbeth), 241-282. New York: Cambridge University Press.

Organic forms of carbon are also present in the ocean. Their dominant source is the photosynthetic fixation of CO_2 by algae in the sunlit surface waters. The resulting growth of the phytoplankton is kept in balance by grazing species. Dissolved organic carbon compounds (hydrocarbons, aromatic compounds, carbohydrates, organic acids, etc.) are produced by the decay of dead cells and by direct release of these molecules by phytoplankton. The ocean probably acts as a source of several hydrocarbons and other organic compounds, which affect the chemical composition of the atmosphere (see *Hydrocarbons in the Atmosphere*). Figure 3 presents a schematic representation of the carbon cycle in the ocean.

In the euphotic zone (well-lit upper layers of the ocean), dissolved inorganic carbon (DIC) is converted to calcium carbonate ($CaCO_3$) and organic carbon. This material is transported to the aphotic zone (dark layers of the ocean) and to the sediments by particle setting and by ocean circulation. In these deep layers, carbonate calcium is dissolved by chemical and biological processes, while organic carbon is remineralized to DIC. DIC is transported to the upper ocean layers in regions, where upwelling is intense.

1.2. Terrestrial Carbon Processes and Surface Fluxes

Exchanges of carbon and oxygen between the terrestrial biosphere and the atmosphere result from photosynthesis and respiration by plants. While the mechanisms involved are composed of a multitude of elementary reactions, the sum of these processes is generally expressed by single stoichiometric reactions. For example the assimilation of CO_2 by plants through photosynthesis is represented stoichiometrically by:

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad (6)$$

where CH_2O represents organic matter. The corresponding gross influx of CO_2 from the atmosphere to the biosphere is referred to as gross primary production (GPP). A fraction of the carbon is reemitted by the plants to the atmosphere through (autotrophic) respiration processes, which in stoichiometric form, can be expressed by the inverse reaction:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad (7)$$

The net carbon flux, that is, the accumulation of carbon in the phytomass, is called net primary production (NPP). It represents all the carbon stored in leaves, branches, and roots of plants. When vegetation is eaten, much of the organic matter is oxidized back to CO_2 in respiration. When plants or animals die, the material is decomposed (oxidized) by microorganisms, and CO_2 is remineralized and released to the atmosphere. Over a long time period, respiration of this organic matter (heterotrophic respiration) approximately balances net primary production. Figure 4 provides a schematic overview of the global carbon cycle in relation to the continental biosphere.

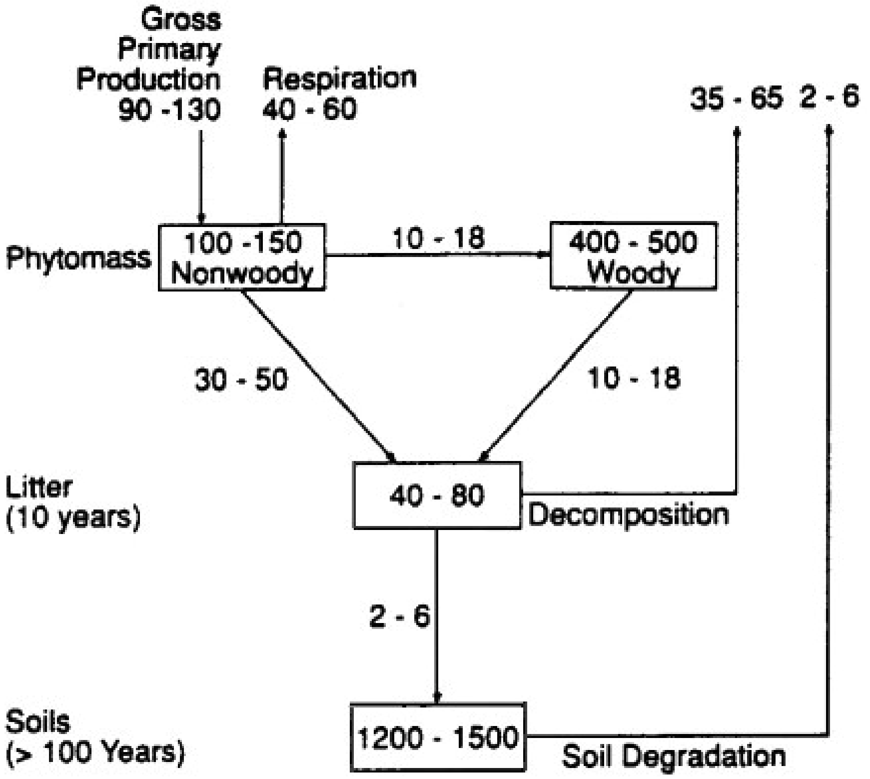

Figure 4. Carbon cycle in the continental biosphere. Reservoirs and fluxes are expressed in GtC and GtC y^{-1}, respectively.
Fung I. (1993). Models of organic and terrestrial sinks of anthropogenic CO_2. In: Biochemistry and Global Change, (ed. R.S. Oremland), New York: Chapman and Hal.

The terrestrial system is currently acting as a global sink for carbon despite large releases of carbon due to deforestation in some regions. Likely mechanisms of this sink are affected by several factors such as changes in land use and management which affect the amount of carbon in plant biomass and soils. Land cleaning can occur, leading to soil degradation, erosion and leaching of nutrients, and may reduce the subsequent ability of the ecosystem to act as a carbon sink. Ecosystem conservation and management practices can restore, maintain, and enlarge carbon stock. Fire is important in the carbon budget of some ecosystems and is affected directly by management and indirectly by land-use change. Fire is a major short term source of carbon, but adds to a small longer-term sink through production of slowly decomposing and inert black carbon.

Deforestation has been responsible for almost 90 percent of the estimated emissions due to land use change since 1850, with 20 percent decrease of the global forest area. Deforestation appears to be slowing slightly in tropical countries and some deforested areas in Europe and North America have been reforested in recent decades. Managed or regenerated forests generally store less carbon than natural forests, even at maturity. Analysis of scenarios for future development show that expanded use of biomass energy could reduce the rate of atmospheric CO_2 increase. It has been estimated that slowing down deforestation and promoting natural forest regeneration and afforestation could increase carbon stocks, mostly in the tropics.

Peat lands/wetlands are large reserves of carbon, because anaerobic soil conditions and low temperatures reduce decomposition and promote accumulation of organic matter. Anaerobic decomposition releases methane (CH_4) which has a global warming potential (see *Greenhouse Gases and Global Warming*) about 23 times that of CO_2. Draining peat lands for agriculture increases total carbon released by decomposition, although less is in the form of methane. Forests grown on drained peat lands may be sources of sink for CO_2 depending on the balance of decomposition and tree growth.

Conversion of natural vegetation to agriculture is a major source of CO_2, not only due to losses of plant biomass but also, increased decomposition of soil organic matter caused by disturbance and energy costs of various agricultural practices. The use of fertilizers, irrigation, residue management and reduced tillage can reduce losses and enhance uptake within managed areas. These processes have led to an estimated increase of soil carbon in agricultural soils.

Climate can lead to changes in the carbon balance. Solar radiation, temperature and available water affect photosynthesis. Warming may increase annual plant growth in temperate and arctic ecosystems where it can increase the length of the seasonal and daily growing cycles, but it may decrease the annual plant growth in water-stressed ecosystems as it increases water loss. Changes in rainfall affect plant water availability and the length of the growing season. Cloud cover can be beneficial to annual plant growth in dry areas with high solar radiation, but detrimental in areas with low solar radiation. Changing climate can also affect the distribution of plants and the incidence of disturbances such as fire, wind, insect and pathogen attacks, leading to changes to the carbon accumulated by biomass.

Other factors that affect the mechanisms of the terrestrial carbon sink are: the increase of atmospheric CO_2 (described in detail later), the anthropogenic nitrogen deposition, the change in atmospheric chemistry.

2. Carbon Monoxide

2.1. Sources and Chemistry of Carbon Monoxide

Carbon monoxide (CO) is a colorless, odorless, neutral, gaseous oxide, which is highly poisonous. It is slightly soluble in water, but is soluble in ethanol and benzene. It has melting point -205.1 ºC and boiling point -191.5 ºC

Carbon monoxide is produced whenever organic matter is burnt in a limited quantity of oxygen. For this reason it is found in the exhaust gases of motor vehicles, as well as in cigarette smoke. The reaction of steam with red-hot coke (900 ºC) also produces carbon monoxide with hydrogen gas (H_2). This mixture of CO and H_2 is called water gas and is used as an industrial fuel:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \quad (8)$$

Because carbon monoxide burns readily in oxygen with a blue flame to produce carbon dioxide:

$$2CO + O_2 \rightarrow 2CO_2 \quad (9)$$

it is useful as gaseous fuel. It is also useful as a metallurgical reducing agent because at high temperatures it reduces many metal oxides to the elemental metal. For example, copper (II) oxide, CuO and iron (III) oxide, Fe_2O_3 are both reduced to the metal by carbon monoxide:

$$CuO + CO \rightarrow Cu + CO_2 \quad (10)$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \quad (11)$$

Natural sources of carbon monoxide include CO from biomass burning and the oxidation of organics such as methane and isoprene, CO from biological processes in soils, CO from vegetation and termites, and CO from the ocean. Carbon monoxide does not absorb terrestrial infrared radiation strongly enough to be counted as a direct greenhouse gas, but its role in determining tropospheric hydroxyl radicals indirectly affects the atmospheric burden of methane and can lead to formation of ozone.

The residence time of carbon monoxide in the atmosphere is of the order of 4 months. It is generally agreed that carbon monoxide is removed from the atmosphere by reaction with hydroxyl radical ($HO\bullet$):

$$CO + HO\bullet \rightarrow CO_2 + H \quad (12)$$

The reaction produces hydroperoxyl radical as a product:

$$O_2 + H + M \rightarrow HOO\bullet + M \quad (13)$$

where M are energy-absorbing species, usually molecules of oxygen (O_2) or nitrogen (N_2). $HO\bullet$ is generated from $HOO\bullet$ by the following reactions:

$$HOO\bullet + NO \rightarrow HO\bullet + NO_2 \quad (14)$$

$$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2 \quad (15)$$

The latter reaction is followed by photochemical dissociation of hydrogen peroxide (H_2O_2) to regenerate hydroxyl radical ($HO\bullet$):

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet \quad (16)$$

Soil microorganisms act to remove CO from the atmosphere. Therefore, soil is a sink for carbon monoxide.

-
-
-

Bibliography

Birks J.W., Calvert J.G., Sievers R.E. (eds) (1993). *The Chemistry of the Atmosphere: Its Impact on Global Change: Perspectives and Recommendations,* 170 pp. Washington, DC: American Chemical Society. [This book is a collection of the recommendations and lectures of the CHEMRAWN VII conference. It addresses the problem of protecting the earth's atmosphere from damage that results from human activities. Viewpoints of science, industry, and developing countries are presented, and the theme of international cooperation is emphasized.]

Brasseur G.P., Orlando J.J., Tyndall G.S. (eds) (1999). *Atmospheric Chemistry and Global Change*, 654 pp. New York: Oxford University Press. [This book presents an integrated examination of chemical processes in the atmosphere, focusing on global scale problems and their role in the evolution of the earth system.]

Finlayson-Pitts B.J., Pitts J.N. (2000). *Chemistry of the Upper and Lower Atmosphere*, 969 pp. New York: Academic Press. [This book is the most comprehensive and modern account of atmospheric chemistry currently available. It examines in depth the current knowledge of the atmosphere with emphasis on the chemical and physical interactions between the troposphere and the stratosphere.]

IPCC (2002). Davidson O., Metz B., Co-Chairs, (2002). *Proceedings of Workshop on Carbon Dioxide Capture and Storage*, 106 pp. Published by ECN. [Intergovernmental Panel on Climate Change (IPCC) was jointly established by the World Meteorological Organisation and the United Nations Environment Programme. The proceedings contain the revised, completed and updated versions of the papers presented during the workshop on carbon capture and storage.]

IPPC (2001). Houghton J.T., Ding Y., Griggs D.J., Noguer M., Van der Linden P.J., Dai X., Maskell K., Johnson C.A. (eds) *Climate Change 2001: The Scientific Basis. Contribution of Working Group I of the Intergovernmental Panel on Climate Change*, 881pp. New York: Cambridge University Press. [This report is a very comprehensive and up-to-date scientific assessment of past, present and future climate change. It analyses an enormous body of observations of all parts of the climate system, it catalogues increasing concentrations of atmospheric greenhouse gases, it projects scenarios of future climate change using a wide range of models of future emissions of greenhouse gases and aerosols, it makes a detailed study of whether a human influence on climate can be identified.]

Manahan S.E. (2000). *Fundamentals of Environmental Chemistry*, 989 pp. New York: Lewis Publishers. [This book provides the reader with little or no background in chemistry with the fundamentals of chemistry and environmental chemistry need for a trade, profession, or curriculum of study that requires a basic knowledge of these topics.]

Schwedt G. (2001). *The Essential Guide to Environmental Chemistry*, 268 pp. New York: John Wiley & Sons. [This book outlines the problems and issues facing the environmental chemist throughout the ecosystem, providing a concise overview of environmental pollution in air, water and soil. The book also includes a chapter on strategies for environmental analysis.]

US EPA (2002). *Greenhouse Gases and Global Warming Potential Values, Excerpt from the Inventory of*

US Greenhouse Emissions and Sinks: 1990-2000, 16 pp. www.epa.gov/globalwarming/publications/emissions [The Inventory of U. S greenhouse emissions and sinks presents estimates by the United States government of U. S anthropogenic greenhouse gas emissions and removals for the years 1990 through 2000.]

Biographical Sketches

Panayotis A. Siskos is Professor of Analytical Chemistry and Environmental Analysis at the National and Kapodistrian University of Athens. He is also Head of the Environmental Analysis Group of Environmental Chemistry Laboratory. Professor Siskos has focused his research activities for the last 20 years on Atmospheric Chemistry and Environmental Pollution. The last five years his research interests also include Human Exposure, Risk Assessment, Environmental Management, and Green Chemistry. Professor Siskos is the author of the book "Atmospheric Chemistry" (in Greek) and Co-Author of the books: "Analytical Separation Methods" (in Greek) and "Clinical Chemistry" (in Greek). He has also translated the book "Quality Assurance of Chemical Measurements" of John Keenan Taylor (Lewis Publishers). He has published more than 75 research papers in refereed journals, 60 papers in proceedings and 30 technical and review papers on various fields of analytical chemistry and environmental analysis. Professor Siskos is a national representative in the Division of "Chemistry and Environment" of FECS (Federation of European Chemical Societies) and the Green Chemistry Institute, coordinator of the committee on Environment of the Hellenic Organization for Standardization (ELOT). He has also served as national expert to the European Collaboration Action Committee "Indoor Air Pollution and its impacts on man" (DGXII- European Union).Member of the Mediteranean Network for Green Chemistry (MEGREC)

Polyxeni P. Georgiou is a chemist with Master's degree in "Chemistry and Environmental Technology". Presently she is working in the industrial sector as a Quality Manager. Mrs. Georgiou has focused her research activities on Pesticides, Fertilizers, Environmental Pollution and Quality Control Systems. More precisely she has worked on: development of analytical methods for the determination of pesticides residues in fruits and vegetables, determination of physicochemical characteristics of pesticide formulations, determination of macronutrients in fertilizers, determination of volatile organic compounds (VOC's) in the atmosphere of indoor places and examination of wastewater.