IV. GAS AND AEROSOL FLUXES

Christopher S. Martens

A. Introduction

Atmospheric chemical processes are intimately linked to hydrospheric pro-
cesses through the transfer of gases and aerosols. These transfers, or fluxes,
are defined as the material transport per unit area per unit time. There is a
growing realization that, through the addition of energy or materials, mankind
has the capability to significantly alter the chemical composition of the atmo-
sphere and the heat budget of the Earth (e.g., Kellogg, 1978). For example,
increasing emissions of fluorocarbons for which the stratosphere appears to be
the major sink, may lead to significant depletion of stratospheric ozone in the
decades ahead (Singh et al., 1979).

Unfortunately we lack adequate data concerning global distributions and
fluxes of both man-made and natural materials important in resolving these
problems as well as understanding natural geochemical cycles. For example, the
sources, sinks, and atmospheric lifetime of N_2O are not well understood
(Liu et al., 1977). Its role in stratospheric ozone depletion as well as the
nitrogen cycle therefore remains uncertain. Another example is the uncertainty
in sea-salt aerosol production rates. Recent tropospheric budgets for materials
such as arsenic (Walsh et al., 1979) include estimates of sea-salt production
rates (e.g., Eriksson, 1959) which have high uncertainties.

The global scale need for accurate distribution and flux determinations
for such materials represents a major problem area potentially amenable to
applications of remote sensing technology.

In the following sections discussions of three priority problem areas
are presented:

(1) Trace gas fluxes;

(2) Sea-salt aerosol production; and

(3) Effect of sea surface microlayer on gas and aerosol fluxes.

Discussions of trace gas fluxes are emphasized because of their potentially key
role in the stratospheric ozone depletion hypothesis. Secondary emphasis is
placed on the latter two topics because of their significance in geochemical
budgets and association with air-sea interface processes. Included in the
trace gas section is a brief discussion of gas flux measurement methodology.

B. Trace Gas Fluxes

Volatile sulfur, carbon, nitrogen, and halocarbon compounds will be con-
sidered in this section. A statement of the problem associated with each com-
pound or group of compounds, brief summary of our current understanding, and
suggestions for needed research will be presented for each. The term
"hydrosphere" is broadly defined to include waterlogged soils.

1. Gas Flux Measurements Techniques

Gas fluxes from soils have generally been measured with open-bottomed chambers which either seal off a volume of air over a known soil area (closed chamber) or are partially open to continual artificially induced or filtered air flow across the soil surface (open chamber; see Matthias et al., 1978, for review). Gas fluxes are deduced from concentration changes in closed chambers. Gas concentration differences between entering and leaving air or build-up in an in-line collection system can be utilized to determine fluxes in open chamber systems.

Open chamber methods similar to those currently in use appear to originate with the work of Pearson et al. (1965) who designed a recirculating, turbulently mixed chamber system for measuring soil radon-222 emanation. Their results suggested the importance of atmospheric turbulence in controlling flux rates, a result confirmed only for coarse soils by Kimball and Lemon (1971). Kanemasu et al. (1974) have since demonstrated a "suction" flux enhancement associated with open chamber measurements, while Matthias et al. (1978) have shown that less disturbance to natural soil gas concentration profiles results from their use.

Both closed and open chamber methods have been used in recent studies of sediment-water fluxes of the dissolved gases methane (King and Wiebe, 1978; Martens and Klump, 1980), and radon-222 (Hammond and Fuller, 1979; Martens et al., 1980).

Air-sea gas fluxes are usually indirectly calculated using the classical stagnant film model of Lewis and Whitman (1924) as described by Broecker and Peng (1974). In this model gas fluxes are assumed to be controlled by molecular diffusion across a thin stagnant film, the log of which has been shown to be linearly proportional to wind speed (Emerson, 1975).

Measurements of vertical gradients in wind speed and gas concentrations can also be utilized to calculate vertical gas fluxes through a horizontal plane using the equation (Lemon and Lemon, 1979):

$$ F = \frac{k^2 (\mu_2 - \mu_1)(c_1 - c_2)}{\left(\ln \frac{z_2}{z_1} \right)^2} $$

where k is von Karman's coefficient, μ is wind speed, c is gas concentration, and z is height.

The methods above provide total flux measurements. Insufficient flux data are available for most gases from which to construct accurate global flux estimates. Consequently, such estimates have been made from interhemispheric tropospheric concentration differences for gases such as methane (Ehhalt, 1977) and CH_3Cl (Jesson et al., 1977; Singh et al., 1979). Assuming an interhemispheric exchange rate of 1 year (Czeplak and Junge, 1974), this technique

is useful for gases with residence times on the order of years. Lodge et al. (1974) have pointed out the lack of applicability of such flux calculations methods to short-lived gases such as H_2S and NH_3.

2. Sulfur

Statement of problem

A major entry in current global sulfur budgets is an, as yet, unidentified flux from the Earth's surface to the atmosphere (Kellogg et al., 1972; Friend, 1973). The dominant site or sites of this flux as well as the most important chemical species involved are not presently known, although the sulfur is thought to be of biogenic origin (Lovelock et al., 1972; Rasmussen, 1974; Hitchcock, 1975; Graedel, 1977; Adams et al., 1979). It is important to address this problem because of the significance of both gaseous and particulate sulfur compounds in both urban and rural environments. In addition, other problems such as the possible importance of carbonyl sulfide (COS) in the formation of the stratospheric sulfate layer (Crutzen, 1976; Sze and Ko, 1979) need to be resolved.

Present understanding

Current global sulfur budgets are in reasonable agreement and suggest that a biogenic flux of approximately 150 ± 75 megatons of sulfur from land and ocean to the atmosphere is required for a balance cycle (Kellogg et al., 1972; Friend, 1973). Until the early 1970's it was generally thought that H_2S was the major biogenic sulfur contribution. Later studies by Lovelock et al. (1972) and Rasmussen (1974) suggested $(CH_3)_2S$ or CH_3SSCH_3 as being more important. Recent studies by Adams et al. (1979) suggest that a larger array of compounds should be considered including CS_2 and COS. The picture is further obscured by oxidation processes. Zinder et al. (1977) report that H_2S and CH_3SH (methyl mercaptan) are the major volatile sulfur compounds produced by algal mats under anaerobic conditions and that CH_3SSCH_3 emitted from such mats may be an oxidation product of CH_3SH. Sze and Ko (1979) have suggested that COS may be an oxidation product of CS_2 or $(CH_3)_2S$ although Graedel (1977) has suggested that SO followed by SO_2 is the most likely product.

Additional complications include physical and biological factors such as temperature dependency of fluxes and condition of biogenic emission sources. For example, Adams et al. (1979) have presented data suggesting that CS_2 is an important emission from injured salt marsh grass. Brinkman and Santos (1974) have suggested that the emission of H_2S from the Amazonian flood plain lakes coincides with the falling water period.

Needed research

A major gap is the lack of quantitative flux measurements for the variety of compounds discussed above. The behavior of the major S species in both the water column and atmosphere is poorly understood. Man's demonstrated impact on the global sulfur cycle (e.g., Kellogg et al., 1972; Berner, 1971) points to a need to locate the sites of fluxes to the atmosphere. When the site(s) and important species are identified, the impact of fluxes on a hemispheric to

14

local scale can be more readily assessed. Measurements of the fluxes of key chemical species across the range of environments from open ocean to coastal are needed.

3. Nitrogen

Statement of problem

The global nitrogen cycle begins with the fixation of atmospheric nitrogen. As an essential nutrient fixed nitrogen is assimilated by organisms, discharged through their subsequent decay or as waste, further recycled through oxidation-reduction reactions, and returned to the atmosphere following denitrification (Delwiche, 1970; Delwiche and Bryan, 1976). The rates of several of these processes are poorly known on a global scale at present. As man's production of N fertilizers increases the question of how the N cycle will adjust must be addressed. Active N compounds in the atmosphere (NO, NO_2, HNO_3, and NH_3) can exert control over gas-phase chemistry and precipitation pH, while N_2O is the source of stratospheric NO_x important in stratospheric ozone chemistry (Crutzen, 1970; 1979).

Present understanding

Reviews in articles by Delwiche (1970), Delwiche and Bryan (1976), and Liu et al. (1977) adequately outline our current understanding of the nitrogen cycle. The rapidly increased usage of industrially produced nitrogen fertilizers (≈ 6 percent per year) should result in increased N_2O production which, according to McElroy et al.'s (1976) predictions, could result in 20 percent reductions of ozone by the year 2025. Liu et al. (1977) have reduced this estimate to a 1 to 2 percent global ozone reduction in the next 50 years, but point out that the sources, sinks, and lifetime of N_2O are not well understood.

Man's production of fixed N is having an impact on coastal waters where N is often the limiting essential nutrient (Ryther and Dunstan, 1971).

Needed research

The results of Liu et al. (1977) and other more recent studies (R. Cicerone, personal communication, 1979) suggest that N_2O production may not offer as great a threat to the stratosphere ozone layer as some other compounds including volatile halocarbons (see below). However, the problem warrants continued study.

Quantification of the global nitrogen cycle will require better estimates of fluxes between the hydrosphere and atmosphere. Determination of oceanic nitrification and denitrification rates remains as a major problem. Other gaps in present understanding include mechanisms of microbially mediated chemical transformation processes in a range of environments from anoxic sediments to aerobic waters as well as surface microlayers. Transport mechanisms for the various gaseous (e.g., N_2, N_2O) and aqueous (e.g., NO_3^-, NH_4^+) species between sedimentary, aqueous, and atmospheric environments must also be further elucidated.

4. Methane

Statement of problem

Tropospheric methane concentration data collected over the past decade (Ehhalt, 1977) appear to suggest a 10 to 15 percent rise. Such a rise would imply significant effects on atmospheric chemical and radiative effects. The sites and magnitudes of methane fluxes for terrestrial and marine methane reservoirs are yet to be delineated.

Present understanding

Calculations of a 10 to 15 percent rise in tropospheric methane concentrations based on an annual 1966-1967 average tropospheric concentration of 1.41 ppmv (Ehhalt and Heidt, 1973) and more recent data yielding concentrations above 1.5 ppmv (e.g., Swinnerton cited in Ehhalt, 1977) may be incorrect (R. Cicerone, personal communication, 1979). The 1966-1967 data appear to be systematically low due to calibration errors; however, there remains evidence for a less significant concentration increase.

Current estimates of the atmospheric lifetime of methane in the troposphere (Ehhalt, 1977; Singh et al., 1979) are based on the interhemispheric concentration difference and calculated production rates between hemispheres. Global methane production can be estimated as the total tropospheric methane concentration divided by the atmospheric lifetime. The production estimate of about 7×10^{14}g methane/yr obtained agrees well with the predicted $5.5 - 10.4 \times 10^{14}$g/yr flux estimate based on extrapolations from various ecosystems (Ehhalt, 1974).

Needed research

The distribution of important flux sites is unknown and therefore a mechanism for any atmospheric increase cannot be identified. Because atmospheric methane concentration variations have important consequences for global atmospheric processes, an understanding of the coupling between production rates and human activities is needed.

5. Halocarbons

Statement of problem

Fluorocarbons and certain chlorocarbons such as methyl chloroform (CH_3CCl_3) have been identified as major potential depleters of stratospheric ozone (Singh et al., 1979, and references therein). Data of Singh et al. (1979) suggest an average annual increase of F-12 (CCl_2F_2) and F-11 (CCl_3F) of 10 and 12 percent, respectively. The implications of increases in these and other fluorocarbons and chlorocarbons are for depletion of stratospheric ozone.

Present understanding

Singh et al. (1979) present the first extensive global measurements of halocarbons which allow for accurate calculations of atmospheric residence times of halocarbons using interhemispheric tropospheric concentration differences and emissions data. Results for F-12 and F-11 suggest residence times of 65 to 70 and 40 to 45 years, respectively, ruling out the missing sinks suggested by Lovelock et al. (1973) on the basis of earlier data. F113 (CCl_2FCClF_2) and F114 ($CClF_2CClF_2$), also man-made and emitted primarily in the northern hemisphere, appear to have stratospheric sinks.

CH_3CCl_3, with a tropospheric residence time of about 8 to 10 years (Singh et al., 1979), appears to be increasing at a rate of 17 percent annually in agreement with worldwide emission increases. An estimated 15 to 20 percent of the total should enter the stratosphere. Based on tropospheric and surface ocean concentrations the ocean is inferred to be a source of CH_3Cl.

Needed research

Further global data sets and studies of the tropospheric residence times and emissions of halocarbons are needed in order to assess the impact of man-made emissions on stratospheric ozone. The fluorocarbon compounds may be used as tracers for global circulation while more reactive compounds such as CH_3CCl_3 may be used for quantifying the role of the hydroxyl radical (HO) in cleansing the atmosphere (Singh et al., 1979).

C. Sea-Salt Aerosol Production

Statement of problem

It is believed that the major source of airborne sea-salt particles is bursting bubbles (Blanchard and Woodcock, 1957). The total production estimate of 1000×10^{12}g/yr (Eriksson, 1959) used in current tropospheric budget calculations (e.g., Walsh et al., 1979) is based on estimated removal rates which are assumed to equal the production rate. It is also assumed that precipitation removal is equal to calculated dry fallout over the sea. We need more accurate estimates of sea-salt particle production.

Present understanding

Eriksson's (1959) calculated production rates are still in use. Quantitative data concerning the concentration of sea-salt aerosol in various ocean regions is becoming available (e.g., Lovett, 1978). Correlations between airborne sea-salt concentrations and wind speed (Woodcock, 1953; Blanchard and Syzdek, 1972; Lovett, 1978) are in good agreement and aerosol residence times on the order of 12 to 25 hours have been calculated.

Needed research

It should be possible, with adequate global wind speed data and/or direct aerosol concentration determinations, to improve estimates of total airborne

sea-salt inventories. The combination of better inventory and mean residence times could yield improved sea-salt aerosol production estimates.

D. Sea Surface Microlayer Problem

Statement of problem

Sea surface microlayers, surface films, or "slicks" are known to play a role in gas and aerosol exchange between the hydrosphere and atmosphere (see MacIntyre, 1974, and Liss, 1975, for reviews). Recently the role of microlayers in horizontal chemical transport of materials in estuaries has been elucidated (Pellenbarg and Church, 1979). We know little about the overall geochemical significance of surface microlayers because of restricted sampling capabilities.

Present understanding

Sea surface microlayers, surface films, or "slicks" are known to influence wind speeds near the air-sea interface (Barger et al., 1970), sea-salt particle production (Garrett, 1968; Paterson and Spillane, 1969), and chemical transport processes (e.g., MacIntyre, 1974; Liss, 1975; Pellenbarg and Church, 1979). Thickness of the microlayer is thought to be 100 μm or less (Liss, 1975). The enrichment of organic materials, certain metals, and other compounds in microlayers (e.g., Piotrowicz et al., 1972) may account for differential chemical transport between the hydrosphere and troposphere. Horizontal chemical transport by surface microlayers has also been shown to be important in salt marsh trace metal cycling (Pellenbarg and Church, 1979). Current sampling techniques include stainless steel or plastic mesh, which remove the upper 300 μm, drum "skimmers" which roll over the surface picking up the upper 60 to 100 μm, bubble microtomes, and glass plates or slides which pick up surface films when dipped vertically (see Liss, 1975). The mesh and drum samplers sample 100 ± 50 μm thick samples whereas the bubble microtome and slide methods sample much thinner layers. None of the techniques are well suited for large-scale studies of surface microlayer distribution especially under poor weather conditions.

Needed research

The development of remote sensing techniques addressing almost any aspect of the surface microlayer problem would help to open the way for improved understanding of their overall significance and role in geochemical processes.

E. References

Adams, D. F., S. O. Farwell, M. R. Pack and W. L. Bamesberger. 1979. Preliminary measurements of biogenic sulfur-containing gas emissions from soils. J. Air Pollut. Cont. Assoc. 29: 380-383.

Barger, W. R. and W. D. Garrett. 1970. Effects of an artificial sea slick upon the atmosphere and the ocean. J. Appl. Met. 9: 396-400.

Berner, R. A. 1971. Worldwide sulfur pollution of rivers. J. Geophys. Res. 76: 6597-6600.

Blanchard, D. C. and L. Syzdek. 1972. Variations in Aitken and Giant Nuclei in marine air. J. Phys. Oceanogr. 2: 255-262.

Blanchard, D. C. and A. H. Woodcock. 1957. Bubble formation and modification in the sea and its meteorological significance. Tellus 9: 145-158.

Brinkman, W. L. F. and U. De M. Santos. 1974. The emission of hydrogen sulfide from Amazonian flood plain lakes. Tellus 26: 261-267.

Broecker, W. S. and T.-H. Peng. 1974. Gas exchange rates between air and sea. Tellus 26: 21-35.

Crutzen, P. J. 1970. The influence of nitrogen oxides on the atmospheric ozone content. Quart. J. Royal. Met. Soc. 96: 320-325.

Crutzen, P. J. 1976. The possible importance of CSO for the sulfate layer of the stratosphere. Geophys. Res. Letters 3: 73.

Crutzen, P. J. 1979. The role of NO and NO_2 in the chemistry of the troposphere and stratosphere. Ann. Rev. Earth Planet. Sci. 7: 443-472.

Czeplak, G. and C. E. Junge. 1974. Studies of interhemispheric exchange in the troposphere by a diffusion model. Adv. Geophys. 18B: 57-72.

Delwiche, C. C. 1970. The nitrogen cycle. Sci. Amer. 23: 137-146.

Delwiche, C. C. and B. A. Bryan. 1976. Denitrification. Ann. Rev. Microbiol. 30: 241-262.

Ehhalt, D. H. 1974. The atmospheric cycle of methane. Tellus 26: 58-70.

Ehhalt, D. H. 1977. The CH_4 concentration over the ocean and its possible variation with latitude. Tellus 30: 169-176.

Ehhalt, D. H. and L. E. Heidt. 1973. Vertical profiles of CH_4 in the troposphere and stratosphere. J. Geophys. Res. 78: 5265-5271.

Emerson, S. 1975. Gas exchange in small Canadian Shield lakes. Limnol. Oceanogr. 20: 754-761.

Eriksson, E. 1959. The yearly circulation of chloride and sulfur in nature; Meteorological, geochemical and pedological implications. Part I. Tellus 11: 375-403.

Friend, J. P. 1973. The global sulfur cycle, pp. 177-201. In (S. I. Rasool, ed.). Chemistry of the Lower Troposphere. Plenum, N.Y.

Garrett, W. D. 1968. The influence of monomolecular surface films on the production of condensation nuclei from bubbled seawater. J. Geophys. Res. 73: 5145-5150.

Graedel, T. E. 1977. The homogeneous chemistry of atmospheric sulfur. Rev. Geophys. Space Phys. 15: 421-428.

Hammond, D. E. and C. Fuller. 1979. The use of radon-222 to estimate benthic exchange and atmospheric exchange rates in San Francisco Bay. In (T. J. Conomas, ed.) San Francisco Bay, the Urban Estuary. A.A.A.S., Washington (in press).

Hitchcock, D. R. 1975. Dimethyl sulfide emissions to the global atmosphere. Chemosphere 3: 117-138.

Jesson, J. P., P. Meakin and L. C. Glasgow. 1977. The fluorocarbon-ozone theory-II. Tropospheric lifetimes - an estimate of the tropospheric lifetime of CCl_3F. Atmos. Environ. 11: 499-508.

Kanemasu, E. T., W. L. Powers and J. W. Sij. 1974. Field chamber measurements of CO_2 from soil surface. Soil Sci. 118: 233-237.

Kellogg, W. W. 1978. Influence of mankind on climate. Ann. Rev. Earth Planet. Sci. 7: 63-92.

Kellogg, W. W., R. D. Cadle, E. R. Allen and E. A. Martell. 1972. The sulfur cycle. Science 175: 587-596.

Kimball, B. A. and E. R. Lemon. 1971. Air turbulence effects upon soil gas exchange. Soil Sci. Soc. Amer. Proc. 35: 16-21.

King, G. M. and W. J. Wiebe. 1978. Methane release from soils of a Georgia salt marsh. Geochim. Cosmochim. Acta 42: 343-348.

Liu, S. C., R. J. Cicerone and T. M. Donahue. 1977. Sources and sinks of atmospheric N_2O and the possible ozone reduction due to industrial fixed nitrogen fertilizers. Tellus 29: 251-263.

Lemon, E. R. and D. Lemon. 1979. Nitrous oxide in fresh waters of the Great Lakes Basin. In (C. C. Delwiche, ed.) Denitrification, Nitrification and Atmospheric N_2O. Wiley and Sons, N.Y. (in press).

Liss, P. S. 1975. Chemistry of the sea surface microlayer, pp. 197-243. In (J. P. Riley and G. Skirrow eds.) Chemical Oceanography, Vol. 2, 2nd ed. Academic Press, N.Y.

Lodge, J. P., P. A. Machado, J. B. Pate, D. C. Sheesley and A. F. Wartbarg. 1974. Atmospheric trace chemistry in the American humid tropics. Tellus 26: 250-253.

Lovelock, J. E., R. J. Maggs and R. A. Rasmussen. 1972. Atmospheric dimethyl sulphide and the natural sulfur cycle. Nature 237: 452-453.

Lovelock, J. E., R. J. Maggs and R. J. Wade. 1973. Halogenated hydrocarbons in and over the Atlantic. Nature 241: 194-196.

Lovett, R. F. 1978. Quantitative measurement of airborne sea-salt in the North Atlantic. Tellus 30: 358-364.

MacIntyre, F. 1974. Chemical fractionation and sea surface microlayer properties, pp. 245-299. In (E. D. Goldberg, ed.) The Sea, Vol. 5. Wiley, N.Y.

Martens, C. S., G. W. Kipphut and J. V. Klump. 1980. Coastal sediment-water exchange processes traced by in situ radon-222 flux measurements. Science (to be published Apr. 1980).

Martens, C. S. and J. V. Klump. 1980. Biogeochemical cycling in a coastal basin 1. Methane sediment-water exchange processes. Geochim. Cosmochim. Acta 44: 371-390.

Matthias, A. D., D. N. Yarger and R. S. Weinbeck. 1978. A numerical evaluation of chamber methods for determining gas fluxes. Geophys. Res. Letters 5: 765-768.

McElroy, M. B., J. W. Elkins, S. C. Wofsy and Y. L. Yung. 1976. Sources and sinks for atmospheric N_2O. Rev. Geophys. Space Phys. 14: 143-150.

Paterson, M. P. and K. T. Spillane. 1969. Surface films and production of sea-salt aerosol. Quart. J. Roy. Met. Soc. 95: 526-534.

Pearson, J. E., D. H. Rimbey and G. E. Jones: 1965. A soil-gas emanation measurement system used for radon-222. J. Appl. Met. 4: 349-356.

Pellenbarg, P. E. and T. M. Church. 1979. The estuarine surface microlayer and trace metal cycling in a salt marsh. Science 203: 1010-1012.

Piotrowicz, S. R., B. J. Ray, G. L. Hoffman and R. A. Duce. 1972. Trace metal enrichment in the sea surface microlayer. J. Geophys. Res. 77: 5253-5254.

Rasmussen, R. A. 1974. Emission of biogenic hydrogen sulfide. Tellus 26: 245-260.

Ryther, J. H. and W. M. Dunstan. 1971. Nitrogen, phosphorus and entrophication in the coastal marine environment. Science 171: 1008-1013.

Singh, H. B., L. J. Salas, H. Shigeishi and E. Scribner. 1979. Atmospheric halocarbons, hydrocarbons, and sulfur hexafluoride: Global distributions, sources and sinks. Science 203: 899-903.

Sze, N. D. and M. K. W. Ko. 1979. Is CS_2 a precursor for atmospheric COS? Nature 278: 731-732.

Walsh, P. R., R. A. Duce and J. L. Fasching. 1979. Considerations of the enrichment, sources and flux of arsenic in the troposphere. J. Geophys. Res. 84: 1719-1726.

Woodcock, A. H. 1953. Salt nuclei in marine air as a function of altitude and wind force. J. Met. 10: 362-371.

Zinder, S. H., W. N. Doemel, and T. D. Brock. 1977. Production of volatile sulfur compounds during the decomposition of algal mats. Appl. Environ. Micro. 34: 859-860.