Journal of Atmospheric Chemistry **43:** 195–229, 2002.
© 2002 *Kluwer Academic Publishers. Printed in the Netherlands.*

The Production of Methanol by Flowering Plants and the Global Cycle of Methanol

I. E. GALBALLY [1] and W. KIRSTINE [2]

[1] *CSIRO Division of Atmospheric Research, PMB 1 Aspendale, Vic 3195, Australia, e-mail: ian.galbally@csiro.au*
[2] *School of Applied Sciences, Monash University, Churchill, 3842, Australia, e-mail: wayne.kirstine@sci.monash.edu.au*

(Received: 10 November 2001; in final form: 2 May 2002)

Abstract. Methanol has been recognised as an important constituent of the background atmosphere, but little is known about its overall cycle in the biosphere/atmosphere system. A model is proposed for the production and emission to the atmosphere of methanol by flowering plants based on plant structure and metabolic properties, particularly the demethylation of pectin in the primary cell walls. This model provides a framework to extend seven sets of measurements of methanol emission rates to the global terrestrial biosphere. A global rate of release of methanol from plants to the atmosphere of 100 Tg y^{-1} is calculated.

A separate model of the global cycle of methanol is constructed involving emissions from plant growth and decay, atmospheric and oceanic chemical production, biomass burning and industrial production. Removal processes occur through hydroxyl radical attack in the atmosphere, in clouds and oceans, and wet and dry deposition. The model successfully reproduces the methanol concentrations in the continental boundary-layer and the free atmosphere, including the inter-hemispheric gradient in the free atmosphere. The model demonstrates a new concept in global biogeochemistry, the coupling of plant cell growth with the global atmospheric concentration of methanol. The model indicates that the ocean provides a storage reservoir capable of holding at least 66 times more methanol than the atmosphere. The ocean surface layer reservoir essentially buffers the atmospheric concentration of methanol, providing a physically based smoothing mechanism with a time constant of the order of one year.

Key words: biogeochemical cycle, global budget, methanol, pectin, plant growth, ocean surface layer.

1. Introduction

Although it has been known for some time that methanol is emitted by fruits (Nursten, 1970) and seeds (Fisher *et al.*, 1979), methanol was only recently quantified as a significant volatile from the leaf tissue of flowering plants (MacDonald and Fall, 1993; Nemecek-Marshall *et al.*, 1995; Kirstine *et al.*, 1998; Fukui and Doskey, 1998). The magnitudes of these emissions are less than the emissions of isoprene from plant leaves, but greater than those of monoterpenes. Other sources of atmospheric methanol are from biomass burning (Holzinger *et al.*, 1999; Yokel-

son *et al.*, 1999), plant decay (Warneke *et al.*, 1999), chemical reactions in the atmosphere and ocean (Elliott and Rowland, 1995; Singh *et al.*, 2000), and from anthropogenic activities (Singh *et al.*, 1995; Singh *et al.*, 2000).

Methanol has been confirmed as a widespread constituent of the global atmosphere, with high concentrations in the surface air of rural regions (Goldan *et al.*, 1995a; Riemer *et al.*, 1998; Lamanna and Goldstein, 1999), and lower concentrations at mountainous sites (Goldan *et al.*, 1995b; Goldan *et al.*, 1997; Leibrock and Slemr, 1997). In the free troposphere, its concentration decreases gradually from the mid-latitudes of the Northern Hemisphere to low latitudes of the Southern Hemisphere (Singh *et al.*, 1995). Anthropogenic sources lead to enhanced mixing ratios in urban areas (Snider and Dawson, 1985; Goldan *et al.*, 1995b).

Methanol is apparently one of the most significant organic compounds in the atmosphere, having an annual atmospheric carbon turnover that is exceeded only by methane and isoprene. Methanol is a substantial sink for hydroxyl radicals in the troposphere, next only to methane, carbon monoxide and isoprene. Depending on the prevailing NO_x concentrations, its reaction and reaction products will either act as net radical sinks (low NO_x), or to enhance the concentrations of oxidising species (NO_x rich). While there has been pioneering work by Singh *et al.* (2000) on the atmospheric cycle of methanol, neither the sources of atmospheric methanol, nor its full environmental cycle, have been adequately quantified. In this paper, we present a new model to explain and quantify methanol emissions from flowering plants. We then include this biological model in a larger model of the environmental cycle of methanol in the global atmosphere and oceans, and estimate the contribution of a range of natural and anthropogenic processes to atmospheric and oceanic concentrations of methanol.

The assumption used throughout is that the global biospheric processes involved in the methanol cycle have a well-defined steady state that is appropriate to recent decades. Given that recent studies indicate that the biosphere and atmosphere are currently undergoing significant long-term change (Houghton *et al.*, 1999; Prinn *et al.*, 2001), this is probably not entirely true. However, the assumption of steady state is reasonable for an initial study of a new biogeochemical coupling, as undertaken here.

2. Materials and Methods

Two models are presented in this paper. They are (a) Model I: the model of methanol production in growing plants, and (b) Model II: the model of the cycle of methanol in the biosphere, atmosphere and ocean. To explore the influence of natural variability in the input parameters on the two model outputs Monte Carlo propagation of uncertainty simulations were performed with the steady state solutions of the models using @Risk software (Palisade Corporation, California U.S.A.). Each of the input parameters is allowed to vary over its observed maximum range in the plant, terrestrial, atmospheric and oceanic environment, causing

Table I. Model parameters used for computing the methanol emission from higher plants. Parameter ranges, based on literature data, are given in parentheses

Parameter	Symbol	Suggested values for parameters	
		Type I cell wall	Type II cell wall
Fraction of cell dry mass that is cell wall	F_c	0.4 (0.2–0.6)	0.5 (0.4–0.6)
Fraction of cell wall mass that is pectin	F_p	0.35 (0.2–0.4)	0.05 (0.03–0.07)
Fraction of pectin that is methylated	F_m	0.5 (0.2–0.8)	0.5 (0.2–0.8)
Fraction of pectin demethylated during elongation	F_d	0.1 (0.05–0.2)	0.1 (0.05–0.2)
Mass of methanol per mass of pectin monomer	K	0.16	0.16

a variation in the output variables: emissions for Model I, and concentrations and removal rates for Model II. The natural variabilities of the input parameters are presented in Table I for the plant model, Model I, and in the Appendix for the environmental model, Model II. In many cases, there are inadequate data to define the statistical distributions of those parameters. Therefore, we have represented each input parameter by a triangular probability distribution with the observed average value, and our best estimate of the maximum and minimum values based on observations and physical constraints. It is assumed in this analysis that errors are uncorrelated. The output errors are related to input errors through the transformations in the models. In some cases, where the model output is weakly sensitive to an input parameter, a large input uncertainty is transformed into a smaller uncertainty in the output, and vice versa.

Throughout the paper when the source, sink or storage of methanol is quantified, the mass units reflect the full molecular mass of methanol unless otherwise specified. Commonly, plant composition measurements are made relative to the dry matter content of the plant and this applies throughout this paper unless otherwise specified.

2.1. BIOSYNTHESIS OF METHANOL IN PLANTS

The synthesis of methanol in flowering plants is associated with the stabilisation of pectin in the plant cell walls (Fall and Benson, 1996). In order to justify the structure of the model that we subsequently present, it is necessary to review these processes.

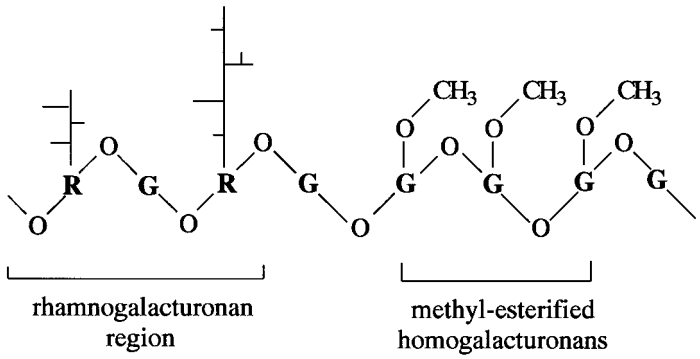

Figure 1. Portion of a pectin polymer chain. G represents galacturonic acid, R denotes rhamnose, and the solid branched lines are arabinogalactan side-chains.

Each growing cell of a flowering plant is encased by a primary cell wall that serves as the structural material of the plant, as well as a regulator of the intercellular transfer of macromolecules (Bacic *et al.*, 1988; McCann and Roberts, 1991). Two distinct types of cell walls have been identified (Carpita and Gibeaut, 1993). Most plants possess a type I primary cell wall in which about half the dry mass consists of cellulose microfibrils interlocked by the hemicellulose, xyloglucan. About 35% of the dry mass of type I cell walls consists of pectin (Fry, 1988; Cosgrove, 1997). While the cellulose/hemicellulose network, along with small amounts of structural proteins, forms the main skeletal framework of the cell, the pectin matrix acts as the binding mechanism to hold the structure together (McCann and Roberts, 1991; Carpita and Gibeaut, 1993). The nature of the bond between adjacent pectin polymers determines the plasticity and rigidity of the cell wall, and controls wall pore size.

Some monocotyledons, in particular the grasses (family Poaceae), have a type II primary cell wall in which cellulose is bound by glucuronoarabinoxylans instead of xyloglucans, ether linkages predominate over ester linkages, and the pectin content is significantly reduced (Bacic *et al.*, 1988; Carpita and Gibeaut, 1993; Carpita, 1996). In spite of these differences, both type I and type II cell walls exhibit similar growth mechanisms (Carpita and Gibeaut, 1993).

The structure of pectin polymers is variable among plant species, and even within the tissues of the same plant. However, most pectins contain significant amounts of polygalacturonic acid (PGA), a homopolymer of α-D-[1 $\rightarrow$ 4]-galactosyluronic acid units with varying degrees of methyl esterification. As shown in Figure 1, these blocks of galactosyluronic acid units are interspersed with branched rhamnogalacturonan formed from alternating L-rhamnosyl and D-galactosyluronic acid residues (McNeil *et al.*, 1984; Carpita and Gibeaut, 1993).

Pectin molecules are formed in the early stages of cell development in an unesterified or partially esterified form (Doong *et al.*, 1995). Subsequent methyl

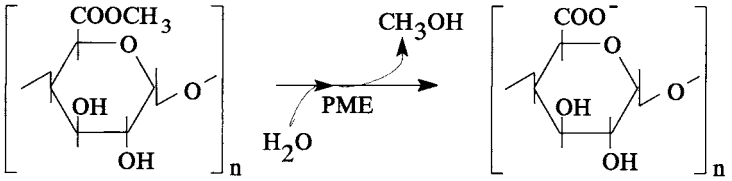

Figure 2. Formation of methanol from pectin.

esterification of the PGA chain inhibits the formation of cross-links between contiguous strands, and increases the fluidity of the pectin matrix.

Cells grow by elongation of the primary cell wall. This elongation not only requires the addition of more strands of cellulose and hemicellulose, but also the continual adaptation of the pectin matrix. As new cellulose microfibrils are formed, cross-linking of the pectin molecules must be reduced to allow the pectin matrix to increase in plasticity, yet still maintain the cell wall integrity. This can happen through methylation of the PGA. Following extension, the PGA is demethylated through the action of the enzyme, pectin methylesterase (PME), to give ionised galacturonic acid residues and methanol as shown in Figure 2. This is the process that leads to methanol release from the plant's leaf to the atmosphere. The other consequence of the demethylation is that the negative charge of the ionised galacturonic acid attracts metal ions such as Calcium (Ca^{2+}), which are common in the plant tissue (Nari *et al.*, 1991; Moustacas *et al.*, 1991). Although other types of bonding may also be important, the pectin matrix is stabilised primarily by blocks of contiguous ionised galacturonate residues that are cross-linked by Ca^{2+} bridges (Demarty *et al.*, 1984; Jarvis, 1984). These cross-links are able to form in the absence of methyl esterification or recurrent side-chains, and have the effects of increasing cell wall rigidity and hindering cell wall extension (Grant *et al.*, 1973). As a consequence, methanol emissions from plant leaves are much higher when the leaves are young and expanding than when they reach maturity (MacDonald and Fall, 1993; Nemecek-Marshall *et al.*, 1995).

A number of other experiments have shown that the demethylation of pectin by PME quantitatively liberates methanol from plant cell walls (McFeeters and Armstrong, 1984; Mangos and Haas, 1997; Frenkel *et al.*, 1998). We suggest, therefore, as an extension of the arguments of Fall and Benson (1996), that most of the methanol emitted from vegetation is quantitatively linked to the process of pectin demethylation by the enzyme, pectin methylesterase (as shown in Figure 2), and that this reaction is the fundamental process for methanol production by higher plants. Small, but probably insignificant, amounts of methanol may be formed in conjunction with the protein repair pathways (Mudgett and Clarke, 1993), or by demethylation of DNA (Finnegan *et al.*, 1998).

2.2. MODEL I: METHANOL PRODUCTION AND ITS EMISSION BY FLOWERING PLANTS

Here we propose a quantitative model to relate the process of plant growth to the amount of methanol released from the plant to the atmosphere. This model builds on the qualitative descriptions of this process that have preceded this paper (Fall and Benson, 1996; Kreuzwieser *et al.*, 1999; Singh *et al.*, 2000), and a preliminary quantitative estimate by ourselves (Kirstine and Galbally, 1998). It is assumed that the only significant source of methanol from growing plant tissue is the demethylation of the pectin contained in the primary cell wall. The mass of methanol emitted from a plant over a given time period can then be calculated by determining the fraction of the net primary production that consists of pectin, and the fraction of this pectin that is demethylated during the process of plant growth. We make the assumption that each of the key processes is independent of the others and contributes linearly to the production. No doubt, as more information becomes available, this model will be improved upon, but we propose that an assumption of linearity is a logical first approximation.

The emission of methanol by plants during growth (E_p) is estimated using the model:

$$E_p = K \sum_i NPP_i (F_c F_p F_m F_d)_i \,, \tag{1}$$

where E_p = emission of methanol from plants over a given period of time; NPP_i = net primary production of plant type i; F_c = fraction of dry biomass that is primary cell wall; F_p = fraction of primary cell wall mass that is pectin; F_m = fraction of pectin that is methylated; F_d = fraction of methylated pectin that is demethylated following cell elongation; and K = mass of methanol produced per mass of pectin monomer that is demethylated.

Few measurements of these fractions are available in the literature for specific plant species. A distinction is made between grasses and other flowering plants, on the basis that the type II primary cell walls of grasses have $F_p \approx 5\%$ (Fry, 1988; Jarvis *et al.*, 1988; Ishii, 1997), compared to $F_p \approx 35\%$ for plants with type I cell walls (Fry, 1988; Ishii, 1997; Cosgrove, 1997). The proportion of the dry biomass of higher plants attributable to the primary cell wall, F_c, is variable from species to species, within specimens of the same species, and also among tissues of the same plant. Based largely on measurements by Margan *et al.* (1988) for various forage crops, and Gordon *et al.* (1985) for grasses, we estimate F_c values of 40% and 50% for type I and type II cell walls, respectively. The other fractions included in Equation (1) are assumed, in the first instance, to be representative of all plant species.

The quantitative values of these terms in Equation (1) are derived as follows:

- a review of the literature suggests that the degree of methylation, F_m, of non-fruit plant pectin varies from 20% to 80%, with most measurements being in

the middle of this range (Hayashi *et al.*, 1980; Vreelend *et al.*, 1989; McCann *et al.*, 1994; Goldberg *et al.*, 1994; Doong *et al.*, 1995; Femenia *et al.*, 1998). Since little difference appears to exist between type I and type II primary cell walls with respect to degree of methylation (Kim and Carpita, 1992; Goldberg *et al.*, 1994), the value, $F_m \approx 50\%$ is adopted for all plants;

- the percentage of methoxy groups actually converted to methanol in order to allow for the degree of Ca^{2+} bonding necessary to stabilise the cell wall, F_d, is difficult to estimate. The value of F_d was estimated at approximately 10%, based on the results of experiments by Morris *et al.* (1980) involving variations in the strength of pectin gel, and by McCann *et al.* (1994) concerning changes in the pectin ester content of tobacco suspension cells during elongation;
- since the methoxy group has a fractional mass of 31/191 relative to the mass of the pectin monomer, K is equal to 16%.

The typical values of the available measurements of these plant biochemical parameters are summarised as fractions in Table I. The emission of methanol is calculated by substitution of these values into Equation (1). The ratio of methanol carbon emission to net primary carbon production estimated by this model is $0.024 \pm 0.008\%$ for grasses and $0.11 \pm 0.03\%$ for other higher plants.

One of the strengths of this model is that it can be applied to estimate methanol emissions at any scale from single leaves up to the entire planetary biomass. As is evident from the above review of parameters, there is not yet sufficient information about any one individual plant species to unequivocally predict its methanol emission ratio. Only emission ratios averaged over multiple plant species could be calculated.

2.2.1. *The Cycle of Methanol within Leaves and Its Release to the Atmosphere*

The methanol produced in flowering plants can have several fates. It can be stored in water and tissue within the plant, it can diffuse out through stomata to the atmosphere, or it can be oxidised to formaldehyde by methanol oxidase. A conceptual model to illustrate these processes is shown in Figure 3. The following analysis, based on observations of methanol in the leaves of plants (Nemecek-Marshall *et al.*, 1995), provides some insight into questions concerning the storage, vapour pressure and high turnover rate of methanol within leaves.

The methanol content of bean leaves has been measured as 10 to 27 μg g^{-1} (fresh mass) for old and young leaves, respectively (Nemecek-Marshall *et al.*, 1995). These figures would be at least three times higher when expressed per unit dry mass. The leaf methanol emissions measured by Nemecek-Marshall *et al.* (1995) were such that, if the emission rate remained constant and no new methanol were produced, all of the methanol in the leaf would be lost to the atmosphere in three hours. This gives an indication of the turnover rate of methanol in

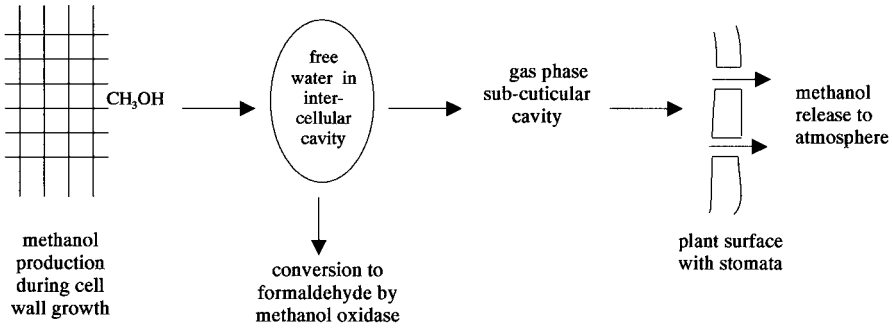

Figure 3. The release of methanol from within the leaf.

leaves. Stomatal resistance may be an important controlling influence on methanol emissions.

Methanol is relatively insoluble in the leaf cuticle material that makes up the surfaces of leaves (Merk and Riederer, 1997); hence we neglect this as a sink region. The incidence of methylotrophic bacteria on the leaves of plants is 1×10^4 organisms per cm^2 (Corpe and Rheem, 1989), and this represents a coverage of between 0.01% and 0.1% of the leaf surface area. Given that the methanol that these bacteria consume must diffuse through the air to the bacteria, and that there is the competing pathway of unrestricted diffusion of methanol away from the leaf into the free atmosphere, simple scaling calculations suggest that it is unlikely that methylotrophic bacteria are a significant sink for methanol. These conclusions are also supported by the observations of methylotrophs on leaf surfaces made by Fall (1996).

Presumably, a portion of the methanol within the leaf will be oxidised to formaldehyde, and ultimately to carbon dioxide. The occurrence of methanol metabolism has been observed in sycamore cell cultures (Gout *et al.*, 2000). Unfortunately, this latter process has not been quantified for intact plants and therefore cannot be included in our model. Consequently, the best assumption at this stage (until there are studies of methanol oxidation in intact plants) is that the large majority of the methanol produced in the leaf escapes to the free atmosphere.

2.3. MODEL II: THE ENVIRONMENTAL CYCLE OF METHANOL

The simple environmental model that we have developed is aimed at exploring the physical and chemical constraints on the global cycle of methanol in a situation where few data are available for verification, but where model predictions that are based on physical and chemical constraints provide new insight into the cycle of this important organic molecule. The model has six compartments, or reservoirs (three in each hemisphere) that each contain the processes for production, storage and removal of methanol, as well as exchange with the other reservoirs. These compartments encompass:

- the continental planetary boundary-layer, along with the continental terrestrial surface including the biosphere and human activities on land;
- the free atmosphere and the marine boundary-layer; and
- the ocean surface layer.

Methanol is moderately soluble in water, with a Henry's law coefficient at 25 °C of 220 mol L^{-1} atm^{-1} (Seinfeld and Pandis, 1998). Thus this model includes consideration of clouds, rainfall and the ocean surface layer, as well as terrestrial and atmospheric processes.

The model is constrained by conservation of mass, current knowledge of the chemical kinetics and solubility of methanol, and trace gas exchange in the biosphere/atmosphere/ocean system. The relevant constants and parameters are presented in Table II. The components of the model are described in the following sections.

2.3.1. *The Terrestrial Sources of Methanol*

The terrestrial sources of atmospheric methanol described here are: plant emissions, plant decay, biomass burning and industrial production. The total sources, E_T, can be represented as emissions by:

$$E_T = \sum_j E_j \,, \tag{2}$$

where E_j is the jth terrestrial methanol source.

The methanol emissions from plant growth have been discussed earlier. The emissions from plant decay are described here. From the derivation of these emissions in the following sections, it is apparent that all except the industrial sources are linearly related to, either the global net primary production, *NPP*, of plants, or their heterotrophic respiration, R_h. We use the empirical approximation that biomass burning is a form of heterotrophic respiration; many models of the global biosphere implicitly make this assumption. Thus, the global terrestrial source term for methanol is written as:

$$E_T = NPP \sum_i F_i \cdot G_i + R_h \sum_i F_i \cdot G_i + E_I \,, \tag{3}$$

where F_i = fraction of the global *NPP*, or R_h, that is involved with process i; G_i = methanol emission factor per unit of biomass growth or decay for process i; and E_I = global industrial emissions of methanol.

This equation is used in the subsequent model of the environmental cycle of methanol.

Table II. Values of parameters used in the global environmental model of methanol

Name	Units	N.H.	S.H.	Reference
Net primary productivity	g(C) y^{-1}	5.64×10^{16} (global)	5.64×10^{16} (global)	Field *et al.* (1998)
Hemispheric fraction of NPP		0.624	0.376	Cao and Woodward (1998)
Fraction of NPP that is grass	g(C)/g(C)	0.34	0.34	Field *et al*. (1998)
Leaf biomass	g	7.50×10^{16} (global)	7.50×10^{16} (global)	Box (1981)
Carbon content of biomass	g g^{-1}	0.45	0.45	Vitousek *et al.* (1986)
Water in ocean surface layer	L	1.24×10^{19}	1.65×10^{19}	Using 80 m as depth
Moles of air in troposphere	mol	7.09×10^{19}	7.09×10^{19}	
Henry's law constant at 298 K	mol L^{-1} atm^{-1}	220	220	Seinfeld and Pandis, 1998
Henry's law constant at other temperatures, e.g., 288 K	mol L^{-1} atm^{-1}	389	389	Using $\Delta H/R = -4881$

2.3.2. *The Release of Methanol from Dead Plant Material*

Plant material has many different fates. Of the global net primary production of 125 Pg y^{-1} estimated by Field *et al.* (1998), around half the carbon that is fixed is transferred underground and ceases to be available as a source of atmospheric methanol; another 18% is eaten by herbivores (Cyr and Pace, 1993); other components are harvested, eaten by grazing animals, burnt or lost into water bodies (Vitousek *et al.*, 1986; Schlesinger, 1997). We estimate that the residual biomass available for above ground decay is approximately 38 Pg y^{-1}.

The methanol in the plant at the time of its death can be released to the atmosphere. Only the methanol content of bean leaves has been recorded in the literature (Nemecek-Marshall *et al.*, 1995), and no information is available for stems or for leaves of other plant species. Based on these limited data, it was estimated that 3.4 Tg of methanol is accumulated within the amount of plant material that dies annually. It is assumed that this methanol is rapidly released to the atmosphere.

There are also two other pathways to methanol formation from dead plant material; these are decay processes that use the cell wall components, pectin and lignin, as substrates.

A number of PME isoforms are found in microorganisms and higher plants that can act in concert to degrade pectin polymers (Hugonvieux-Cottee-Pattat *et al.*, 1996). In addition, pectin methylesterase is capable of remaining active under a wide range of environmental conditions. Some isoforms of PME survive the normal pasteurisation processes employed for bottled fruit juices (Castaldo *et al.*, 1997). While the total pectin content of dead plant material can be estimated, PME may not demethylate all pectin ester groups (Doong *et al.*, 1995). The extent of conversion of pectin methoxy groups to methanol depends on the nature of the pectin and the form of the PME. In general, pectin methylesterases extracted from higher plants remove methyl groups in blocks. In cases where the methyl esters are arranged in blocks within the pectin molecule, removal can be nearly complete, but if the methoxy groups are arranged randomly, the degree of demethylation may be reduced. Since the PME from microbial sources appears to act randomly in removing methoxy groups, the PME from organisms involved in decay processes is more likely to produce higher levels of demethylation (Mangos and Haas, 1997). Massiot *et al.* (1997) found that PME treatment of apple pectin released 65% of the total methanol content of the pectin. This finding is consistent with earlier estimates of a 60–75% conversion (Rexová-Benková and Markovic, 1976).

On the basis of the above information, it seems likely that most of the PME formed by the plant (or produced by microorganisms) remains active under normal environmental conditions, and is capable of demethylating about 65% of the pectin in the tissue of the dead plant. Thus, the potential source of methanol from the pectin of dead plant material can be estimated to be 800 Tg y^{-1}, but only a part of this methanol will be released into the atmosphere. Some of it will dissolve in soil-

water, and given that methanol is readily utilised as a food source by bacteria, much of it will undergo oxidation. Observations are used to constrain these emissions from dead plant material.

The volatile organic compounds released from dead plant material have been studied by Warneke *et al.* (1999), and were found to contain significant amounts of acetone and methanol. The characteristics of these emissions of acetone and methanol were quite different, with strong evidence that the acetone was produced by abiological Maillard reactions (Warneke *et al.*, 1999). We suggest that PME activity may strongly contribute to the methanol release and may explain the distinction between the characteristics of the methanol release and those of the classical Maillard process. Further, the experiments of Warneke *et al.* (1999) were carried out in a warm to hot wet/dry environment. As such, they represent decay processes characteristic of the wet/dry climates such as savannas, mediterranean regions, steppes and deserts. In our model, the release rate of methanol per unit biomass of 3×10^{-4} to 5×10^{-4} g g^{-1}, determined by Warneke *et al.* (1999), is used for biomass decaying in these parts of the world. It is assumed that the release rate of methanol per unit biomass in moister regions of the world will be smaller by a factor of three than that above, largely in response to more effective microbial scavenging of methanol, due both to the more frequent presence of liquid water and to the heavier litter loadings in these environments. Using the division of global ecosystem productivity presented by Guenther *et al.* (1995) and the above emission rates, a global release rate of methanol from decaying plant material via PME activity was determined to be 6.5 Tg y^{-1} (with a range from 2 to 13 Tg y^{-1}).

A second source of methanol during plant decay is the demethylation of lignin during fungal decomposition of wood (Ander and Eriksson, 1985; Kirk and Farrell, 1987). Experiments conducted by Ander and Eriksson (1985) confirmed that the white-rot fungus, *Phanerochaete chrysosporium*, was capable of liberating between 4% and 25% of the lignin mass as methanol under ideal conditions. The lignin content of dead plant material varies from 5% for leaves (van Elsas *et al.*, 1997) to an average of 25% for wood (Kirk and Farrell, 1987), and about 18% of the mass of lignin molecules consists of methoxy groups (Bourbonnais and Paice, 1992). As indicated previously, the biomass available for aboveground decay is 38 Pg y^{-1}. On this basis, lignin decomposition could provide a potential source of about 34 Tg of methanol per year. However, given that this methanol release is inhibited by the presence of oxygen (Ander and Eriksson, 1985; Reid, 1992), it is likely that most of it is oxidised to carbon dioxide and only a small fraction is released to the atmosphere.

Laboratory experiments to determine the methanol production from lignin have been conducted in sealed flasks with carbon to oxygen mass ratios of about 1:40 (Ander and Eriksson, 1985; Reid, 1992). In the global biosphere-atmosphere system, the carbon to oxygen mass ratio (litter to atmospheric oxygen) is of the order of $1{:}10^4$. Given that the samples of Ander and Eriksson (1985) were contained in a constant gas volume, it is assumed that the most appropriate value of the fractional

release of methanol from lignin decomposition from their study is the one that has the smallest ratio of carbon to oxygen. The result is that under natural conditions no more than 10% of the methanol produced from lignin degradation would be released into the atmosphere. Thus, the global release rate of methanol from decaying plant material via lignin decomposition is estimated to be 2.9 Tg y^{-1}, with a range of 1 to 10 Tg y^{-1}. The total methanol production from the dead plant material, either contained in the plant at death or formed from the decomposition of pectin or lignin, is, therefore, 13 Tg y^{-1}, with a range from 5 to 31 Tg y^{-1}.

Potentially, methanol can be produced when methane is generated and oxidised in ruminating animals, rice paddies, wetlands, sewage works and landfills. Methanol (along with formaldehyde and formate) is an intermediate in the methane oxidation process (Haber *et al.*, 1983; Higgins *et al.*, 1984):

$$CH_4 \rightarrow CH_3OH \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2 . \quad (4)$$

Methanol, thus formed, is utilised for growth by methylotrophs, and is readily converted to formaldehyde and then formate, by the enzyme alcohol dehydrogenase. Currently, we have little information on these potential sources of methanol and assume that they are negligible because the microbial processes that are conducive to methanol production are also conducive to methanol consumption, namely, moist environments where methanol exists preferentially in the aqueous phase.

2.3.3. *Emissions of Methanol from Biomass Burning*

Methanol is produced during the smouldering phase of biomass burning, and is associated with anthropogenic activities such as deforestation, shifting agriculture, the use of wood as a fuel, and the destruction of agricultural residues (Crutzen and Andreae, 1990). The methanol is believed to result from the pyrolysis of methyl and methoxy groups found in the lignin and hemicellulose polymers of the biomass (McKenzie *et al.*, 1995). Given that between 1800 and 4700 Tg of carbon (mean = 3300 Tg(C)) from dry biomass are burnt annually (Crutzen and Andreae, 1990), it is expected that biomass burning releases significant amounts of methanol into the atmosphere. The emission ratio of methanol to carbon monoxide is highly variable and has been measured on only a narrow range of materials under laboratory conditions. For example, the methanol released during the combustion of a number of savanna grass species ranged from 0.15% to 8.0% of the release of carbon monoxide (Holzinger *et al.*, 1999). Andreae and Merlet (2001) have recently estimated the global emission of methanol from biomass burning to be 12.7 Tg y^{-1}, being 3.9 Tg y^{-1} from savanna and grassland, 2.6 Tg y^{-1} from tropical forest, 1.3 Tg y^{-1} from extratropical forests, 2.8 Tg y^{-1} from biofuel burning, 0.13 Tg y^{-1} from charcoal making and burning, and 2.1 Tg y^{-1} from the combustion of agricultural residues. For this model, we use a global emission of methanol of 12.7 Tg y^{-1}, as estimated by Andreae and Merlet (2001), with an uncertainty of 50%.

2.3.4. *Industrial Emissions of Methanol*

Global industrial methanol production in 1996 was 24.3 Tg y^{-1}, and projected to increase to 27.2 Tg y^{-1} in 2000 (Crocco, 1997). (The units used in Crocco (1997) are Mt, which are equivalent to Tg.) The expected uses of this 27.2 Tg of methanol are: for the chemical production of other organic compounds such as formaldehyde and MTBE 20.3 Tg; for fuel 0.7 Tg.; as solvent 1.1 Tg; and 5.1 Tg for other purposes. Uses of methanol include: fuel or fuel additives (e.g., MTBE); chemical production (e.g., formaldehyde, acetic acid, chloromethanes, dimethyl terephthalate and methyl methacrylate); as a solvent; an antifreeze; an inhibitor; or as a substrate for microbes involved in single-cell protein production, crop growth and sewage treatment (Crocco, 1994). From this information, the global emission of industrially produced methanol was estimated to be about 3.7 Tg y^{-1}. This determination is consistent with the estimate of anthropogenic methanol emission to the atmosphere of 4 Tg y^{-1} by Singh *et al.* (1995) and 2–4 Tg y^{-1} by Singh *et al.* (2000), based on atmospheric observations.

2.3.5. *Methanol Chemistry in the Atmosphere*

Calculations suggest that methanol has an average chemical lifetime due to gas phase removal of 16 days in the free troposphere (Singh *et al.*, 1995), and a shorter lifetime of 69 daylight hours in the planetary boundary-layer (Jacob *et al.*, 1989). The chief process for removal of atmospheric methanol is oxidation by hydroxyl radicals (·OH) in the gaseous phase (Atkinson, 1985).

$$CH_3OH + \cdot OH \xrightarrow{O_2} HCHO + \cdot HO_2 + H_2O\,. \tag{5}$$

A similar reaction of methanol and hydroxyl radicals occurs in the aqueous phase (Asmus *et al.*, 1973).

To capture the variation of methanol loss rate with the kinetic reaction coefficient and the ·OH concentration at different altitudes and latitudes, the loss rate is calculated separately for the continental boundary-layer and the free atmosphere, and for the gas phase and the aqueous phase of cloud water. The ·OH concentrations used in the gas phase are based on the observations of Prinn *et al.* (2001), which are consistent with recent chemical model calculations (Spivakovsky *et al.*, 2000). Within the free atmosphere, the 8-box approach of Miller *et al.* (1998) (adjusted for the removal of the continental boundary-layer), is used to further ensure that temperature and ·OH covariance is properly represented. Separate calculations are made for the lower (1000–500 hPa) and upper troposphere (500–200 hPa), for low to mid latitudes (0° to 30°) and mid to high latitudes (30° to 90°). The loss rates are then combined to give one representative loss rate for the free atmosphere in each hemisphere.

Cloud droplets provide an aqueous medium for the chemical reaction of methanol with hydroxyl radicals (Monad and Carlier, 1999). In this model, the methanol loss within cloud water is calculated using the ·OH concentration in cloud

water in the remote atmosphere calculated by Lelieveld and Crutzen (1991) and Herrmann *et al.* (2000), and the distribution of cloud water determined by Lelieveld *et al.* (1989). This process takes place in the free atmosphere compartment.

There are also two possible mechanisms for the gas phase production of methanol in the atmosphere:

$$\cdot CH_3O_2 + \cdot CH_3O_2 \rightarrow CH_3OH + \cdot CH_2O + O_2 \tag{6}$$

and

$$HOCH_2CHO + h\nu \rightarrow CH_3OH + CO\,.$$

The reaction products of Equation (6) represent a minor pathway for the loss of methylperoxy radicals by self-reaction (Tyndall *et al.*, 2001). Our calculations of this methanol source, which originates from the oxidation of methane and methyl hydrogen peroxide, provide a value of 18 Tg y^{-1} which agrees with the estimate of Singh *et al.* (2000). The production of methanol from glycolaldehyde is estimated considering the production of glycolaldehyde from isoprene and ethene oxidation, and the removal of glycolaldehyde by hydroxyl attack and photolysis. Kinetic rate constants, yields and the photolysis rate are taken from data in Bacher *et al.* (2001).

2.3.6. *Removal of Methanol by Dry Deposition at Terrestrial Surfaces*

The dry deposition of methanol on terrestrial plant and soil surfaces (in the absence of liquid water) has not been measured. Potentially, it could be a major sink. In some locations a strong diurnal variation in atmospheric methanol is observed (Riemer *et al.*, 1998), but the night-time concentrations remain above the observed concentrations in the free troposphere. In this circumstance, we interpret the diurnal variation in atmospheric concentrations to be the result of the diurnal variation in emissions rather than evidence of a strong surface sink. We estimate the dry deposition velocity of methanol based on a number of considerations, namely, this interpretation of the methanol diurnal variation, the relative insolubility of methanol in the leaf cuticle material that makes up the surfaces of leaves (Merk and Riederer, 1997), the incidence of methylotrophic bacteria on the leaves of plants (Corpe and Rheem, 1989), and the fact that plants are a methanol source. Our estimate is that the dry deposition velocity of methanol on terrestrial plant and soil surfaces (in the absence of liquid water) is around 1 mm s^{-1}. This value, which is also adopted by Singh *et al.* (1995), is about one quarter of the deposition velocity observed for surface-reactive species such as SO_2 and O_3 over plant/soil surfaces (Galbally *et al.*, 1979; Galbally and Roy, 1980), and somewhat greater than the uptake rate of nitric oxide (Seinfeld and Pandis, 1998). The dry deposition removal rate of methanol over land, R_d, is represented by the equation:

$$R_d = A_c v_d \bar{\rho} C_b\,, \tag{7}$$

where A_c = area of the continental surface; v_d = deposition velocity of methanol; $\bar{\rho}$ = molar density of air in mol m^{-3}; and C_b = methanol mixing ratio in the continental boundary-layer.

We assume that the methanol that is dry deposited on soil and plants is consumed by microbial and chemical processes and is permanently lost from the atmosphere. The loss process for methanol following dry deposition will be through methylotrophs that utilise methanol for energy. We surmise that this process will be active in moist litter environments that are conducive to methanol uptake.

2.3.7. *Removal of Methanol by Wet Deposition*

The loss of methanol in rainfall is calculated using the solubility of methanol in water at the temperature of warm clouds, namely 5 °C (Seinfeld and Pandis, 1998) and the methanol concentrations appropriate to the top of the planetary boundary-layer in the continental and oceanic regions. The global mean continental rainfall is set as 800 mm y^{-1} and the global mean oceanic rainfall is set as 1200 mm y^{-1} (Sanderson, 1990). Methanol in rain that falls over the continents is assumed to be lost – oxidised within the soil surface layer in a similar manner to methanol that is dry deposited. Methanol in rain that falls into the ocean provides an input to the oceanic methanol cycle.

2.4. ATMOSPHERE-OCEAN EXCHANGE OF METHANOL

The rate of atmosphere-ocean exchange of methanol (that incorporates both dry deposition and release of material from the underlying ocean) is estimated following Liss and Slater (1974) as:

$$E_{ao} = -E_{oa} = \bar{\rho} A_o k_{ao} (C_a P_a - C_o H^{-1}) , \tag{8}$$

where E_{ao} = net exchange of methanol from the atmosphere to the ocean; A_o = surface area of the ocean; k_{ao} = atmosphere-ocean exchange rate in m s^{-1}; P_a = atmospheric pressure at the ocean surface; C_a = mixing ratio of methanol in air; C_o = oceanic concentration of methanol in mol L^{-1}; and H = Henry′s law coefficient for methanol in water expressed in mol L^{-1} atm^{-1}.

The gaseous exchange of methanol between the atmosphere and the oceans is regulated by two resistances: the resistance to the transfer of methanol from the ocean-atmosphere boundary-layer to the ocean surface, and the resistance to transfer of methanol from the ocean surface to within the surface waters. These resistances are discussed by Liss and Slater (1974) and Liss (1983). We have evaluated each of these resistances for the transfer of methanol from a 10-metre height above the ocean surface to a 1-metre depth below the surface. The conditions representative of the open oceans are: a wind speed of 7.7 m s^{-1}, a roughness length of 2×10^{-4} m, and a friction velocity of 0.29 m s^{-1}. These give an atmospheric resistance to methanol exchange of 90 s m^{-1}, corresponding to a transfer velocity of 1.1×10^{-2} m s^{-1}. The water phase transfer velocity, appropriate for methanol, of 4.4×10^{-5} m s^{-1} was taken from Plass *et al.* (1992). After correcting for solubility, it appears that the atmospheric phase has nearly 40 times the resistance of the aqueous phase, due to the moderate aqueous solubility of methanol. The combined

gas and liquid phase resistance, referenced to atmospheric concentrations, is 109 s m^{-1}, corresponding to a transfer velocity of 9.2×10^{-3} m s^{-1}. This is used in subsequent modelling.

2.4.1. *The Continental Planetary Boundary-Layer*

The major global emissions of methanol occur in the continental boundary-layer, and the concentrations and processes for methanol within this layer are different, both qualitatively and quantitatively, from those of the free atmosphere. Because there is no large methanol source in the marine boundary-layer, its methanol concentration is not substantially different to the free atmosphere; thus, for simplicity, the marine boundary-layer is included in the free atmosphere compartment of the model. The exchange of air containing methanol occurs at the boundary between the continental boundary-layer and the free atmosphere. The methanol mass balance in the continental boundary-layer is expressed as:

$$\frac{dM_b}{dt} = \sum_j E_j - Q_b \sum_i L_i C_b - \tau_{ba}^{-1} Q_b (C_b - C_a)\,, \tag{9}$$

where M_b = number of moles of methanol in the continental boundary-layer; Q_b = number of moles of air in the continental boundary-layer; L_i = first order loss coefficient for sink process i; C_a = mixing ratio of methanol in the free atmosphere; C_b = mixing ratio of methanol in the continental boundary-layer; and τ_{ba} = exchange time between the continental boundary-layer and the free atmosphere, referenced to the mass of the continental boundary-layer.

The boundary-layer is assumed to be 100 hPa thick – approximately 1 km in height. The exchange of air from the continental boundary-layer takes place through three processes: deep convection fed from air in the boundary-layer; continental outflow of boundary-layer air; and overturning of continental boundary-layer air due to the passage of mid-latitude synoptic systems driven by baroclinic instability. The exchange time of the boundary-layer air with the free troposphere in the mid-latitudes due to baroclinic instability has been estimated using a coarse resolution global atmospheric model to be approximately 10 days (Wang and Shallcross, 2000) and has been estimated for all three processes and a surface source to be about 3 days for the United Kingdom using a 13-km grid regional atmospheric model (Donnell *et al.*, 2001). Considering all three processes and their global distributions, we assume the exchange time of boundary layer air with the free atmosphere is 4 days with an uncertainty of a factor of two.

The sink mechanisms within the continental boundary layer include hydroxyl radical abstraction, wet deposition and dry deposition. The continental boundary-layer hydroxyl radical concentration is determined by scaling the available observations in the continental boundary layer (for example, Brandenberger *et al.*, 1998; Holland *et al.*, 1998; Creasey *et al.*, 2001), taking into account diurnal and seasonal effects, to obtain a yearly average concentration of 2×10^6 molecules cm^{-3}.

This value is consistent with that predicted by atmospheric chemical models (Spivakovsky *et al.*, 2000). The hydroxyl radical concentration in the free atmosphere compartment of the model is adjusted so that the globally integrated value for the troposphere (free atmosphere plus continental boundary-layer) is consistent with that observed by Prinn *et al.* (2001).

2.4.2. *The Free Atmosphere and Marine Boundary-Layer Compartment*

The hemispheric atmospheric cycle of methanol is sufficiently short-lived (approximately 2–3 weeks) so that its atmospheric cycle is confined primarily to the troposphere. The mass balance of methanol in the free atmosphere is represented by:

$$\frac{dM_a}{dt} = \tau_{ba}^{-1} Q_b (C_b - C_a) + E_r - Q_a \sum_i L_i C_a - \bar{\rho} A_o k_{ao} (C_a P_a - C_o H^{-1}) \,. \quad (10)$$

The term E_r represents the production of methanol by methylperoxy radical self-reaction and glycolaldehyde photolysis in the atmosphere. The sink processes are hydroxyl attack in both the gaseous and the cloud water phases, and removal by wet deposition through rainfall. There is an exchange of methanol between the free atmosphere and both the continental boundary-layer and the ocean surface layer. As each hemisphere is modelled as a separate compartment, there is an inter-hemispheric exchange that is represented by:

$$E_{ns} = \tau_{ns}^{-1} Q_n (C_{an} - C_{as}) \,, \quad (11)$$

where E_{ns} = exchange of methanol from the Northern to the Southern Hemisphere; n as a subscript represents the Northern Hemisphere; and s as a subscript represents the Southern Hemisphere.

2.4.3. *The Ocean Surface-Layer*

The ocean surface-layer compartment is assumed to be 80 m deep, consistent with the well mixed surface layer of the oceans that is in physical contact with the atmosphere. The mass balance of methanol in the ocean surface layer is:

$$\frac{dM_o}{dt} = E_h + \bar{\rho} A_o k_{ao} (C_a P_a - C_o H^{-1}) - Q_o \sum_i L_i C_o \,, \quad (12)$$

where E_h is the rate of production of methanol from the hydrolysis of methyl halides in the oceans. The oceans contain both source and sink processes for methanol. Elliott and Rowland (1995) have demonstrated that methyl halides can hydrolyse to methanol in ocean water via the reaction:

$$CH_3X + H_2O \rightarrow CH_3OH + H^- + X^+. \quad (13)$$

The rate of production of methanol from CH_3X (X = Cl, Br or I) is calculated taking into account the observed atmospheric concentrations of these species over

the oceans, their solubilities at ambient temperature and the hydrolysis rates from Elliott and Rowland (1995).

The oceans also contain various free radicals and highly reactive species. The species $\cdot OH$, $\cdot CO_3$ and $\cdot Cl_2$ all react rapidly with methanol, resulting in its decomposition (Seinfeld and Pandis, 1998). These three radicals will only occur in the upper levels of the ocean surface layer due to their production mechanisms and short lifetimes. The loss rate of methanol due to hydroxyl radical attack in ocean water is calculated and included in the model. Observed hydroxyl radical concentrations in ocean water average about 2×10^{-18} mole L^{-1} (Mopper and Zhou, 1990). The 1/e light penetration depth in ocean surface water for wavelengths appropriate for hydroxyl radical generation is about 7 m, and the rate constant for the hydroxyl attack on methanol in aqueous solution is 0.98×10^9 L mole^{-1} s^{-1} (Zhou and Mopper, 1990). The resulting lifetime for methanol in the ocean surface layer due to OH attack is nearly a millennium. There are no representative measurements of $\cdot CO_3$ and $\cdot Cl_2$ in ocean surface water. But, as it is generally assumed that hydroxyl radicals are the most active species in the ocean, then, based on the above analysis, methanol is virtually unreactive in the oceans. There may be biological sources and sinks of methanol in the oceans, but no information about these exists.

2.5. SOLVING THE MODEL AND COMPARING IT WITH THE REAL WORLD DATA

The correct comparison of the model outputs with environmental observations requires that the model outputs and inputs (parameterisation and coefficients) be responsive over the spatial and temporal scales over which the observational data are obtained, or that the observational data be averaged over the same spatial and temporal scales as the model. This is difficult to achieve in practice since different model inputs represent different temporal and spatial scales. For example, considering model inputs, the atmospheric $\cdot OH$ concentration has been determined as an average over several years, integrated over the whole hemispheric troposphere (Prinn *et al.*, 2001), whereas the pectin content of cell walls has been determined for a few individual plant species using samples that may represent only 10^{-10}, or so, of the global leaf annual biomass turnover. In the case of the inputs used in this paper, the modelled concentrations represent those within well mixed atmospheric and oceanic reservoirs on a seasonal to yearly time scale.

Little information exists on methanol in the environment for comparison of observations with the seasonal cycle of concentrations from the model; hence, the comparison is done on annual average conditions. The modelled variability of concentration should be similar to, although less than (because of some smoothing), the range of concentrations observed in well-mixed conditions in the real world. Because of the spatial and temporal scale of the model as discussed above, it is impossible for it to represent such local variability as might be observed in the nocturnal boundary-layer in urban and rural atmospheres, and with local $\cdot OH$ concentration variations in the continental boundary-layer.

3. Results and Discussion

The results of the model of methanol production in growing plants, Model I, and the model of the environmental cycle of methanol, Model II, will be separately compared with observations.

3.1. COMPARISON OF MODELLED EMISSIONS FROM PLANTS WITH AVAILABLE OBSERVATIONS AND ESTIMATION OF THE GLOBAL EMISSIONS OF METHANOL FROM THIS PROCESS

Seven data sets of methanol emission rates from flowering plants are available in the literature (MacDonald and Fall, 1993; Das, 1996; Kirstine *et al.*, 1998; Fukui and Doskey, 1998; Holzinger *et al.*, 2000; Baker *et al.*, 2001; Schade and Goldstein, 2001). These observed emissions were analysed to provide the ratio of methanol emission to net primary production in each of the experiments, and these ratios were compared with the equivalent term estimated by the plant emission model. Since net primary production data were not directly provided in all of the papers, it was derived from associated data as described below. The values determined here are the ratios of moles of methanol emitted to moles of carbon dioxide taken up by the plant as net primary productivity.

Using mature leaves under optimum growing conditions, MacDonald and Fall (1993) recorded leaf emissions of methanol of 13.2 ± 4.1 μg g^{-1} h^{-1}, and a range from 1.5 μg g^{-1} h^{-1} up to 45.7 μg g^{-1} h^{-1} from 11 tree and crop species. Although MacDonald and Fall (1993) did not provide measurements of carbon fixation rate per unit of leaf biomass, this carbon fixation rate can be estimated by assuming that the plants were well watered and in a light-saturated environment. For these conditions, the theoretical NPP (taking into account night time respiration) is 5–8 μmol m^{-2} s^{-1} and the leaf density is 30 m^2 kg(C)$^{-1}$ (Ying Ping Wang, personal communication, 2000), giving a dry matter production per unit mass of leaf tissue of 6–10 mg g^{-1} h^{-1}. Using the observed mean methanol emission rate, an average ratio of methanol emission to NPP of 0.16% was determined.

Das (1996) measured the flux of VOCs over a corn crop during a four-day period in May. The average daytime flux of VOCs was equal to 4.8 ± 0.3 mg m^{-2} h^{-1}, and about 75% of this flux was methanol. Since little methanol is produced when leaf stomata are closed, this flux would be typical of about one-third to one-half of the day. This would suggest a methanol emission flux from the corn crop in the range of (4.6 to 25) $\times$ 10^{-3} g(C) m^{-2} d^{-1}. Assuming a growth rate of above-ground biomass for corn of about 40 g m^{-2} d^{-1} (Beadle *et al.*, 1985), half of the NPP above ground, and 45% of the dry biomass consisting of carbon, the total daily growth rate would be about 35.2 g(C) m^{-2} d^{-1}. Thus, the ratio of methanol emitted to NPP was in the range from 0.013% to 0.072% (mean = 0.04%).

Kirstine *et al.* (1998) determined an annual emission flux of volatiles from grass pasture equal to 1900 mg(C) m^{-2} y^{-1}, of which 11%–15% (or 210–290 mg(C) m^{-2} y^{-1}) was methanol; they measured the accumulation of aboveground biomass over

the growing season to be 2300 g m^{-2}. On the assumptions that half the pasture biomass was below ground, and that the dry biomass was about 45% carbon, the total annual accumulation of carbon as biomass would be about 2100 g(C) m^{-2} y^{-1}. Thus, the mean ratio of methanol emitted to pasture NPP was about 0.012%.

Fukui and Doskey (1998) measured an average methanol emission flux of 460 μg m^{-2} h^{-1} from a grassland plot that produced 552 g m^{-2} of dry above-ground biomass between May 6 and August 11. Assuming about 1000 hours of daylight in this growing period, and an equivalent biomass below ground, their biomass accumulated at a rate of about 1.1 g m^{-2} h^{-1}. Using these estimates, the calculated ratio of methanol emitted to grassland NPP was approximately 0.035%.

Holzinger *et al.* (2000) measured the emission rates of methanol from 6 specimens of oak trees (*Quercus ilex*). Methanol emission rates ranged from 26 to 122 nmol m^{-2} min^{-1}, while carbon dioxide assimilation varied from 330 to 638 μmol m^{-2} min^{-1}. These give a ratio of methanol emitted to NPP of 0.02%, with a range of 0.007% to 0.03%.

Baker *et al.* (2001) measured midday summer methanol fluxes with a mean of approximately 0.7 mg(C) m^{-2} h^{-1} (range 0 to 2.4 mg(C) m^{-2} h^{-1}) above a sub-alpine pine forest in the Rocky Mountains of Colorado. For a growing season of about 1000 hours, this would be equivalent to about 0.7 g(C) m^{-2} h^{-1}. Snowy conifers have an NPP of 643 g m^{-2} y^{-1} (Guenther *et al.*, 1995). Therefore as 50% of the tree biomass is carbon, the ratio of methanol emitted to NPP in this ecosystem would be about 0.2%, with an uncertainty of at least 100%.

Schade and Goldstein (2001) measured methanol fluxes from the leaf canopy of a young pine plantation in the Sierra Nevada Mountains in California over a two-month period during the summer. Average daytime fluxes were 1.09 mg(C) m^{-2} h^{-1}, and average night-time fluxes were reduced to 0.25 mg(C) m^{-2} h^{-1}. This is equivalent to a full-day methanol flux of 0.64 mg(C) m^{-2} h^{-1}. Since daytime methanol fluxes were temperature dependent, dropping to about 0.2 mg(C) m^{-2} h^{-1}, winter and autumn emissions would be negligible. The above daily fluxes would be representative of about 5 months of the year, or about 3600 hours. This amounts to a total annual flux of approximately 2.4 mg(C) m^{-2} h^{-1}. As shown by Schade and Goldstein (2001), the biogenic fraction of this flux was about two-thirds of the total, or 1.5 g(C) m^{-2} y^{-1} Assuming an NPP for this ecosystem of 1320 g m^{-2} y^{-1} (Guenther *et al.*, 1995), the ratio of methanol emitted to NPP would be about 0.24%, with an uncertainty of about 50%.

As shown in Table III, the methanol emissions measured by MacDonald and Fall (1993), Das (1996), Fukui and Doskey (1998), Kirstine *et al.* (1998), Holzinger *et al.* (2000), Baker *et al.* (2001) and Schade and Goldstein (2001) indicate a range from 0.01% to 0.24% for the ratio of methanol emission to NPP for various types of higher plants, with values for grass species (including corn) being at the lower end of the range. The independent estimates from our plant model of methanol emissions give a mean of 0.024 $\pm$ 0.008% (min. 0.006%, max. 0.06%) of NPP for grasses, and a mean of 0.11 $\pm$ 0.03% (min. 0.04%, max. 0.24%) for other plants,

Table III. Ratio of carbon emitted as methanol from higher plants to carbon taken up as net primary production, from experimental studies and from the model presented in this paper

Type of vegetation	Methanol/NPP	Reference
Mean of 11 tree and crop species	0.16%	MacDonald and Fall (1993)
6 specimens of *Quercus ilex*	0.02%	Holzinger *et al*. (2000)
Cool pine forest	0.2%	Baker *et al*. (2001)
Pine plantation	0.24%	Schade and Goldstein (2001)
Trees and crops	$0.11 \pm 0.03\%$	Model I, this study
Corn field	0.04%	Das (1996)
Grassland (mixed species)	0.035%	Fukui and Doskey (1998)
Grass pasture	0.012%	Kirstine *et al*. (1998)
Grasses	$0.024 \pm 0.008\%$	Model I, this study

both expressed as moles of methanol per moles of CO_2 fixed. The lower values of methanol emissions observed for grass species, and the fact that the grass species have lower pectin levels associated with type II cell walls, are consistent with the model in that they predict that plants with type II cell walls will produce about one-quarter of the methanol produced by plant species with type I cell walls.

Thus, two approaches to the estimation of methanol emissions from plants have been used here: Model I, based entirely on plant physiology and biochemistry, predicts methanol emission rates, (Table III), that are consistent with completely independent observations of methanol emissions made outside the plant, although the uncertainties in the data from both approaches are quite large.

This model is now used to calculate the emissions of methanol to the global atmosphere by living plants. The global net primary production is estimated by Field *et al.* (1998) to be 125 Pg y^{-1}. The information presented in Cao and Woodward (1998) indicates that 62.4% of the global net primary production is in the Northern Hemisphere and 37.6% is in the Southern Hemisphere. The fraction of net primary production that comes from grasses is 34% (Field *et al.*, 1998). Based on these data, the model of methanol production from flowering plants predicts global emissions of methanol of 10 Tg y^{-1} for grasslands and 90 Tg y^{-1} for other terrestrial plant biomes, giving a total global emission of methanol from flowering plants of approximately 100 Tg y^{-1} (range of 37–212 Tg y^{-1}). There will be a seasonality in methanol emissions that is coupled with the seasonality in plant growth.

Table IV. Southern Hemisphere (S.H.), Northern Hemisphere (N.H.), and global methanol sources with associated uncertainties (minima and maxima). Units: Tg y^{-1}

Sources	S.H.	N.H.	Global
Higher plants	38	62	100 (37–212)
Biomass burning	5	8	13 (6–19)
Atmospheric production	9	10	19 (14–24)
Anthropogenic	1	3	4 (3–5)
Decay of dead plant material	5	8	13 (5–31)
Ocean sources	–	–	<0.1
Total	58	91	149 (83–260)

3.2. THE GLOBAL ENVIRONMENTAL CYCLE OF METHANOL

The sources incorporated in the global environmental model of methanol, Model II, are derived from processes described earlier in this paper, and the source estimates are summarised in Table IV. The model estimate is that 67% of the global emissions of methanol comes from plant growth, and that another 17% of methanol comes from plant decay and biomass burning. Anthropogenic methanol emissions make up 2% of the total emissions to the atmosphere.

The model estimates of the environmental sinks of methanol are presented in Table V. Approximately three-quarters of the methanol emitted into the environment is removed through oxidation by hydroxyl reactions in the atmosphere. The remaining one-quarter of the methanol emitted is removed by deposition and subsequent microbial oxidation in the terrestrial biosphere. The ocean is estimated to be a very minor sink of methanol.

A global budget of methanol has been presented by Singh *et al.* (2000). The major differences with this work are as follows. The budget of Singh *et al.* (2000) does not have a physically based quantitative estimate of the plant growth source of methanol, the major source in this study. The sinks of methanol presented in Singh *et al.* (2000) total only 40 Tg y^{-1} to 50 Tg y^{-1} whereas those here total 149 Tg y^{-1}. The difference between the estimate of methanol destruction by hydroxyl radicals in the atmosphere presented here and Singh *et al.* (1995, 2000) cannot be completely determined. We surmise that the difference may be the consequence of the larger concentration of methanol in the planetary boundary-layer over the continents, as predicted by our model and observed in the atmosphere; see later discussion. The budget of Singh *et al.* (2000) does not include a quantitative estimate of ocean chemical sources and sinks, but these, as evaluated here, are very small.

Table V. Southern Hemisphere (S.H.), and global Northern Hemisphere (N.H.) sink estimates for methanol with associated uncertainties (minima and maxima). Units: Tg y^{-1}

Sinks	S.H.	N.H.	Global
Hydroxyl attack			
(Free atmosphere: gas phase)	29	40	69 (41–128)
(Free atmosphere: cloud water)	2	3	5 (2–15)
(Continental boundary layer)	15	25	40 (19–75)
Wet deposition over land	4	7	11 (5–20)
Dry deposition over land	9	15	24 (11–43)
Chemical and biological destruction in the oceans	0.1	0.2	0.3 (0.2–0.6)
Total	59	90	149 (82–273)

The masses of methanol contained in the various environmental reservoirs as estimated by Model II are: atmosphere 3 Tg; plants 3 Tg; industrial storage 7 Tg; and oceans 230 Tg. The remarkable feature is that, if the water in the ocean surface layer to an 80-m depth is in near-equilibrium with atmospheric methanol as suggested by our model, then this oceanic reservoir contains approximately 230 Tg methanol, more than 66 times the amount in the atmosphere. The oceans represent a large potential reservoir for atmospheric methanol that corresponds to more than a year's emissions of methanol into the environment. This role of the ocean in the global cycle of methanol has not been previously described.

Methanol can pass easily from the atmosphere to the ocean (and vice versa) because of its solubility. As discussed earlier, the rate of atmospheric/oceanic exchange of methanol is very fast, and is limited mainly by the gas phase resistance to the transfer of methanol between the ocean water and the atmosphere. A consequence of this high exchange rate is that the methanol in the atmosphere approaches equilibrium with methanol in the ocean's surface layer with a 90% adjustment time of about 2 weeks. Given that the ocean surface layer contains 66 times more methanol than the atmosphere, the oceans will exert a damping influence on global and hemispheric methanol concentration fluctuations in the atmosphere on a time scale of weeks to a few months. The model estimates methanol concentrations in the ocean surface layer of 0.2 to 0.6 μM (mean= 0.3 μM) in the Northern Hemisphere and 0.1 to 0.4 μM (mean = 0.2 μM) in the Southern Hemisphere. We have not been able to locate any measurements of methanol in ocean water to test our model predictions. Consequently, we have initiated a study to measure methanol concentrations in the Southern Ocean surface layer. Presumably, there is

Table VI. Background atmospheric concentrations of methanol. Units nmol/mol

Region	Concentration	Reference
Rural site, Tennessee	3–22	Riemer *et al*. (1998)
Forest plantation, Alabama	11	Goldan *et al*. (1995a)
Mesa near Boulder, Colorado	1–17	Goldan *et al*. (1995b)
Pine plantation, Sierra Nevada	4–10	Lamanna and Goldstein (1999)
Rural site, near Tucson, Arizona	2.6	Snider and Dawson (1985)
Wank Mountains, Germany	2.3	Leibrock and Slemr (1997)
Rocky Mountains, Colorado	2–6	Goldan *et al*. (1997)
Free troposphere (0–40° N)	0.6	Singh *et al*. (1995)
Free troposphere (0–10° S)	0.4	Singh *et al*. (1995)
Free troposphere (near equator)	0.6	Crutzen *et al*. (2000)

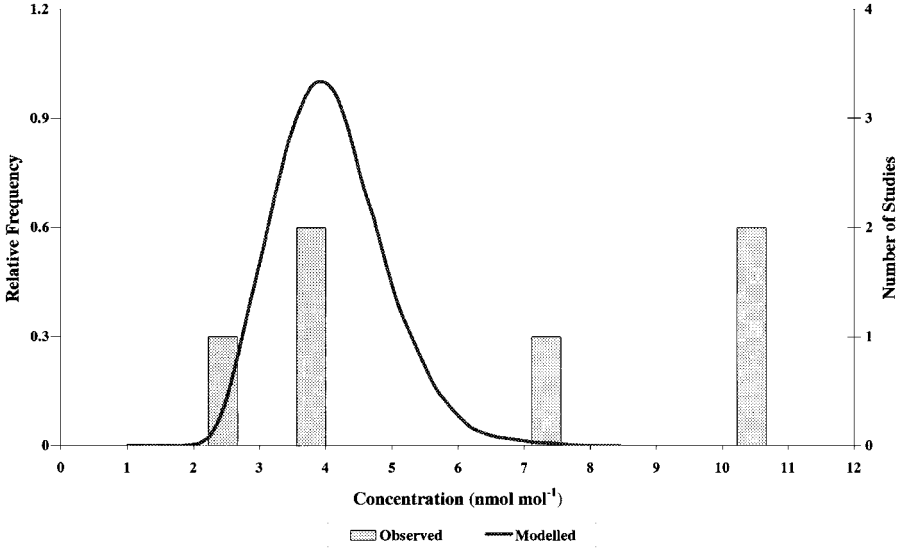

Figure 4. Comparison of the observed average concentrations of methanol in the continental boundary-layer of the Northern Hemisphere from six studies with the equivalent modelled concentrations of methanol represented by a frequency distribution.

also methanol exchange between the ocean surface layer and the deep ocean, but that is beyond the scope of this paper.

The best test currently available for the environmental model is through comparison of estimated annual average concentrations with observed concentrations of methanol in the atmospheric reservoirs. It is important to note that no prior information about these concentrations is incorporated into the model.

The concentrations estimated for the Northern Hemisphere continental boundary-layer and the observed concentrations within this layer are presented in Table VI and in Figure 4. The average concentrations observed in the continental boundary-

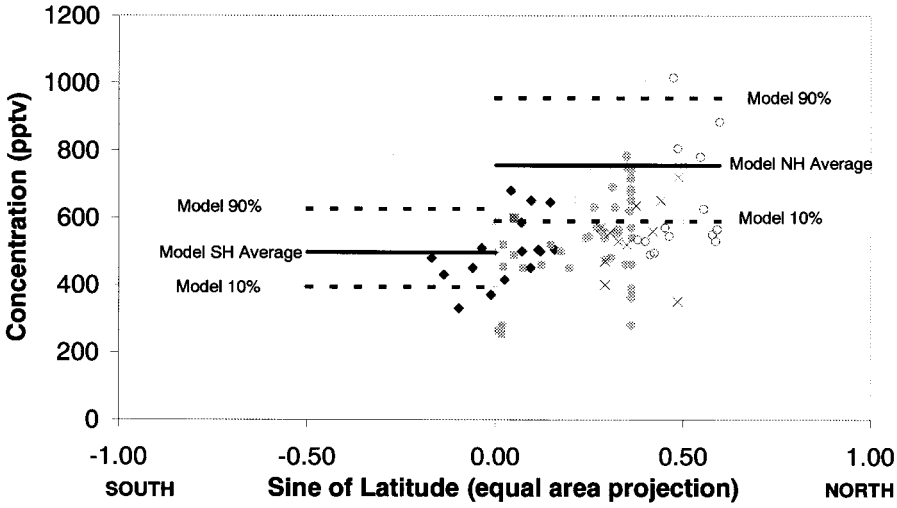

Figure 5. Comparison of the observed and modelled concentrations of methanol in the free atmosphere (including the marine boundary-layer). Observational data are from Singh *et al.* (1995) and Crutzen *et al.* (2000). The modelled concentrations are represented by the mean value and the 10 and 90 percentiles from the uncertainty analysis.

layer and the modelled concentrations, 4 (min. 2, max. 8) nmol mol^{-1} show good agreement, given the independence of the modelled concentrations and the observations. The observed concentrations have higher maximum values, as would be expected because of the spatial and temporal averaging that occurs within the model compared with the real continental boundary-layer. As already discussed, local influences cannot be simulated in this average continental boundary-layer. One key, but poorly known, parameter that has a major influence on concentrations in the continental boundary-layer is the methanol dry deposition rate. No measurements of this rate exist, and such measurements should be undertaken.

The model concentrations estimated for the free troposphere are presented in Figure 5 along with the available data from Singh *et al.* (1995) and Crutzen *et al.* (2000). The model estimates an average concentration in each hemisphere. The pole-to-pole scale used is the sine of latitude, which gives equal areas of the Earth's surface, as well as approximately equal volumes of the atmosphere per unit of sine of latitude. The model concentrations (0.8 nmol mol^{-1} NH and 0.5 nmol mol^{-1} SH) are in good agreement with the atmospheric concentrations and the observed inter-hemispheric gradient. The measured concentrations show a greater variability than the modelled uncertainties, which is expected given that the measurements represent a limited spatial and temporal sampling. In comparison, the modelled concentrations represent the hemispheric annual average concentration and the uncertainty with which it can be predicted from source and sink processes. The methanol concentrations in the free atmosphere in the model are sensitive both to the inclusion/exclusion of the aqueous water phase and to the balance of methanol

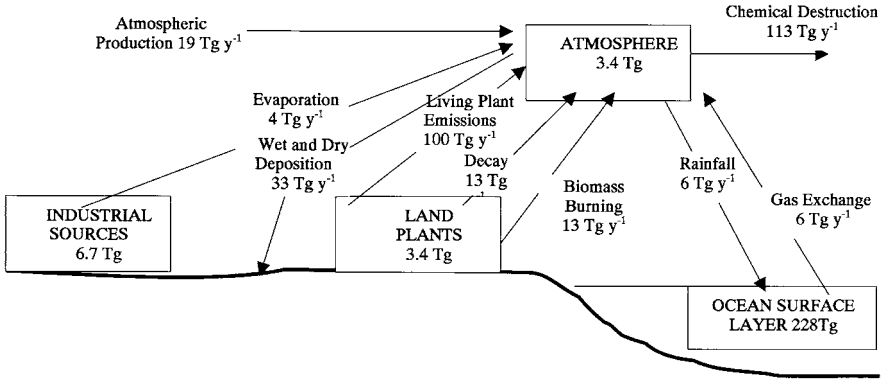

Figure 6. Global biogeochemical cycle of methanol. Boxes represent reservoirs, and arrows represent fluxes.

in the continental boundary-layer. While Crutzen and Lawrence (2000) have shown that wet deposition has only a minor influence on the vertical transport of methanol, the combined effect of clouds (through cloud chemistry), as well as wet deposition, have a major effect on methanol concentrations in the free atmosphere.

The complete cycle of methanol in the global environment is presented in Figure 6. The reservoirs and processes have been discussed already. One interesting aspect of the methanol cycle is that rainwater will provide a net transfer pathway for methanol from the atmosphere to the oceans because of the relationship between solubility and temperature. The average temperature at which rainfall forms is lower than the average ocean surface temperature. This methanol transferred by rainfall to the ocean, in the absence of a significant sink of methanol in the ocean, will be returned to the atmosphere by gas exchange.

There are many substantial uncertainties in these plant emission and global environmental models of methanol presented here. The final uncertainties quoted are a result of a systematic error analysis based on the assumption of uncorrelated errors. Measurements that would substantially improve our understanding of methanol in the environment include:

- a systematic climatology of methanol concentrations in the atmosphere;
- dry deposition measurements;
- methanol concentrations in the surface layers of the ocean in each hemisphere; and
- further measurements of the ratio of methanol emissions to carbon uptake by plants.

Once seasonal variations in atmospheric methanol concentrations have been measured, more exhaustive tests of the model can be undertaken.

A prediction can be made using the current model. Net primary productivity was much lower during the last ice age. Assuming that the major sink process through atmospheric ·OH was comparatively constant, methanol production and

its atmospheric concentration should have been much lower. A study of methanol in ice cores should indicate a decrease in methanol during the last ice age.

4. Conclusions

Recently, methanol has been recognised as an important constituent of the background atmosphere, but little is known about its overall cycle in the biosphere/atmosphere system. A model is proposed for the production and emission to the atmosphere of methanol by flowering plants based on plant structure and metabolic properties, in particular on the demethylation of pectin in the primary cell walls. The methanol production and emission model is validated by comparison with seven sets of methanol emission rates from plants that are independent of any information used in the model. Using this model, in conjunction with an estimate of the global rate of net primary production of plants, a global rate of release of methanol from plants to the atmosphere of 100 Tg y^{-1} is calculated. This represents the largest single source of atmospheric methanol.

A separate model of the global cycle of methanol is constructed involving the terrestrial biosphere, atmosphere and ocean surface layer. The model includes emissions from plant growth and decay, biomass burning, atmospheric and oceanic chemical production and industrial production. The removal processes in the model involve hydroxyl radical attack in the atmosphere, clouds and oceans, as well as wet and dry deposition. The model estimates that the ocean provides a storage reservoir capable of holding 66 times more methanol than the atmosphere. The ocean surface layer reservoir essentially buffers the atmospheric concentration of methanol, providing a physically based smoothing mechanism with a time constant of the order of a year. It is estimated that plant growth and decay produce about 76% of the global release of methanol in the atmosphere, and hydroxyl attack causes about three-quarters of the global methanol removal. The model demonstrates a new concept in global biogeochemistry, the coupling of plant cell growth with the global atmospheric concentration of methanol.

Acknowledgements

We thank John Burrows, Frank Dentner, Maria Kanakidou, Stuart Penkett and Ying Ping Wang for their suggestions on processes in the model. This work was presented at the POET Workshop on *Emissions of Chemical Species and Aerosols into the Atmosphere*, 19–22 June 2001, Paris, France.

Appendix

Table A.I. Uncertainties adopted for the input parameters in model

Quantity	Symbol	Units	Value	Minimum	Maximum
Industrial production					
Methanol emitted to atmosphere	E_i	Tg	3.7	2.8	4.6
Plant production					
Type I biomass that is cell wall	F_c^I		0.4	0.3	0.5
Type II biomass that is cell wall	F_c^{II}		0.5	0.4	0.6
Type I cell wall that is pectin	F_p^I		0.35	0.2	0.45
Type II cell wall that is pectin	F_p^{II}		0.05	0.03	0.1
Pectin that is methylated	F_m		0.5	0.3	0.7
Pectin demethylated to form methanol	F_d		0.1	0.08	0.12
Net primary production (Type I)	NPP^I	g y^{-1}	82.5×10^{15}	74×10^{15}	91×10^{15}
Net primary production (Type II)	NPP^{II}	g y^{-1}	42.5×10^{15}	38×10^{15}	47×10^{15}
Plant decay – pectin					
Carbon in biomass	η_c		0.45	0.4	0.5
Above-ground biomass	F_{ag}		0.5	0.4	0.6
Fraction eaten by herbivores	F_h		0.18	0.16	0.20
Amount burned	Q_b	g (C) y^{-1}	3.25×10^{15}	1.8×10^{15}	4.7×10^{15}
Amount eroded by rivers	Q_e	g (C) y^{-1}	4.0×10^{14}	3×10^{14}	5×10^{14}
Consumed by humans	Q_h	g y^{-1}	8.0×10^{14}	7×10^{14}	9×10^{14}
Amount harvested as wood	Q_w	g y^{-1}	2.2×10^{15}	2.0×10^{15}	2.4×10^{15}
Amount eaten by livestock	Q_{ls}	g y^{-1}	2.2×10^{15}	2.0×10^{15}	2.4×10^{15}
Fraction that is grass	F_g		0.3	0.2	0.4
Conversion factor (leaves)	η_{pl}		0.0004	0.0002	0.0006
Conversion factor (grass)	η_{pg}		0.0001	0.00005	0.00015
NPP fraction in dry climes	F_{dc}		0.3	0.28	0.38
Methanol conversion in wet climes	η_{wc}		0.33	0.23	0.43
Plant decay – lignin					
Fraction of dry biomass that is leaves or grass	F_{l+g}		0.8	0.7	0.9
Lignin fraction in leaves	F_l		0.05	0.04	0.06
Lignin fraction in wood	F_{lw}		0.25	0.15	0.35
Methanol/lignin mass ratio	$C_{m/l}$		0.18	0.17	0.19
Fraction of lignin converted to methanol	F_{mc}		0.04	0.02	0.06
Actual fraction converted	$F_{m/l}$		0.1	0.05	0.2
Biomass burning					
Methanol produced	M_{bb}	Tg	12.7	6.4	19
Fraction in Northern Hemisphere	F_{NH}		0.59	0.44	0.73
Atmospheric loss					
Hydroxyl concentration	$[\mathrm{OH}]_a$	cm^{-3}	9.7×10^5	9.1×10^5	10.3×10^5
Rate constant	k_{OH}	cm^3 s^{-1}	3.1×10^{-21}	3.0×10^{-21}	3.2×10^{-21}
Residence time in continental boundary-layer	τ_{ba}	days	4	3	5
Inter-hemispheric exchange time	τ_{ns}	year	1	0.7	1.8
Dry deposition velocity	v_d	cm s^{-1}	0.1	0.05	0.15
Rainfall over ocean	R_o	m y^{-1}	0.8	0.7	0.9
Rainfall over land	R_c	m y^{-1}	1.27	1.1	1.4
Henry's law constant at 298 K	H	M atm^{-1}	220	200	240
Oceans					
Mean wind speed over ocean	u	m s^{-1}	7.7	7.5	7.9
Roughness length of ocean	z_o	m	2×10^{-4}	1×10^{-4}	3×10^{-4}
von Kármán's constant	κ		0.41	0.39	0.43
Transfer velocity of methanol	k	cm h^{-1}	16	14	18
[OH] in ocean surface water	$[\mathrm{OH}]_o$	mol L^{-1}	2×10^{-18}	1×10^{-18}	4×10^{-18}
Active period for OH attack	T_a	days	0.25	0.2	0.3

References

Ander, P. and Eriksson, K.-E., 1985: Methanol formation during lignin degradation by *Phanerochaete chrysosporium*, *Appl. Microbiol. Biotechnol.* **21**, 96–102.

Andreae, M. O. and Merlet, P., 2001: Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles* **15**, 955–966.

Asmus, K.-D., Mockel., H., and Henglein, A., 1973: Pulse radiolytic study of the site of OH· radical attack on aliphatic alcohols in aqueous solution, *J. Phys. Chem.* **77**, 1218–1221.

Atkinson, R., 1985: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.* **85**, 69–201.

Bacher, C., Tyndall, G. S., and Orlando, J. J., 2001: The atmospheric chemistry of glycolaldehyde, *J. Atmos. Chem.* **39**, 171–189.

Bacic, A., Harris, P. J., and Stone, B. A., 1988: Structure and function of plant cell walls, in J. Priess (ed.), *The Biochemistry of Plants: A Comprehensive Treatise*, Volume 14 (Carbohydrates), Academic Press, San Diego, pp. 297–371.

Baker, B., Guenther, A., Greenberg, J., and Fall, R., 2001: Canopy level fluxes of 2-methyl-3-buten-2-ol, acetone, and methanol by a portable relaxed eddy accumulation system, *Environ. Sci. Technol.* **36**, 1701–1708.

Beadle, C. L., Long, S. P., Imbamba, S. K., Hall, D. O., and Olembo, R. J., 1985: *Photosynthesis in Relation to Plant Production in Terrestrial Environments*, Tycooly Publishing, Oxford, p. 47.

Bourbonnais, R. and Paice, M. G., 1992: Demethylation and delignification of kraft pulp by *Trametes versicolor* laccase in the presence of 2,2′-azinobis-(3-ethylbenzthiazoline-6-sulphonate, *Appl. Microbiol. Biotechnol.* **36**, 823–827.

Box, E. O., 1981: Foliar biomass: data BASF of the international biological program and other sources, in J. J. Bufalini and R. R. Arnts (eds), *Atmospheric Biogenic Hydrocarbons*, Volume 1, Ann Arbor Science, pp. 121–148.

Brandenberger, U., Brauers, T., Dorn, H.-P., Hausmann, M., and Ehhalt, D. H., 1998: In-situ measurements of tropospheric hydroxyl radicals by folded long-path laser absorption during the field campaign POPCORN, *J. Atmos. Chem.* **31**, 181–204.

Cao, M. and Woodward, F. I., 1998: Net primary and ecosystem production and carbon stocks of terrestrial ecosystems and their responses to climate change, *Global Change Biol.* **4**, 185–198.

Carpita, N. C. and Gibeaut, D. M., 1993: Structural models of primary cell walls in flowering plants: consistency of molecular structure with physical properties of the walls during growth, *Plant J.* **3**, 1–30.

Carpita, N. C., 1996: Structure and biogenesis of the cell walls of grasses, *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **47**, 445–476.

Castaldo, D., Loiudice, R., Laratta, B., Giovane, A., Quagliuolo, L., and Servillo, L., 1997: Presence of residual pectin methylesterase activity in thermally stabilized industrial fruit preparations, *Lebensm.-Wiss. u.-Technol.* **30**, 479–484.

Corpe, W. A. and Rheem, S., 1989: Ecology of the methylotrophic bacteria on living leaf surfaces, *FEMS Microbiol. Ecol.* **62**, 243–250.

Cosgrove, D. J., 1997: Assembly and enlargement of the primary cell wall in plants, *Annu. Rev. Cell Dev. Biol.* **13**, 171–201.

Creasey, D. J., Heard, D. E., and Lee, J. D., 2001: OH and HO_2 measurements in a forested region of north-western Greece, *Atmos. Environ.* **35**, 4713–4724.

Crocco, J. R., 1994: Global outlook: supply, demand, and marketing, in W.-H. Cheng and K. Kung (eds), *Methanol Production and Use*, Marcel Dekker, New York, pp. 283–317.

Crocco, J. R., 1997: World methanol demand forecast to grow 2.7% over five years, *Hydrocarbon Process.* **76**, 25.

Crutzen, P. J. and Andreae, M. O., 1990: Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles, *Science* **250**, 1669–1678.

Crutzen, P. J. and Lawrence, M. G., 2000: The impact of precipitation scavenging on the transport of trace gases: a 3-dimensional model sensitivity study, *J. Atmos. Chem.* **37**, 81–112.

Crutzen, P. J., Williams, J., Pöschl, U., Hoor, P., Fischer, H., Warneke, C., Holzinger, R., Hansel, A., Lindinger, W., Scheeren, B., and Lelieveld, J., 2000: High spatial and temporal resolution measurements of primary organics and their oxidation products over the tropical forests of Surinam, *Atmos. Environ.* **34**, 1161–1165.

Cyr, H. and Pace, M. L., 1993: Magnitude and patterns of herbivory in aquatic and terrestrial ecosystems, *Nature* **361**, 148–150.

Das, M., 1996: Trends, photochemistry, and analysis of volatile organic compounds in the lower troposphere of the southeastern United States, PhD Thesis, Raleigh, North Carolina.

Demarty, M., Morvan, C., and Thellier, M., 1984: Calcium and the cell wall, *Plant Cell Environ.* **7**, 441–448.

Donnell, E., Fish, D., and Thorpe, A., 2001: Quantifying the export of pollutants from the boundary layer, in S.-E. Gryning and F. A. Schiermeier (eds), *Air Pollution Modeling and Its Application IV*, Kluwer Academic/Plenum Publishers, New York, pp. 183–192.

Doong, R., Liljebjelke, L. K., Fralish, G., Kumar, A., and Mohnen, D., 1995: Cell-free synthesis of pectin, *Plant Physiol.* **109**, 141–152.

Ehrlich, H. L., 1996: *Geomicrobiology*, 3rd edn, Marcel-Dekker, New York.

Elliott, S., and Rowland, F. S., 1995: Methyl halide hydrolysis rates in natural waters, *J. Atmos. Chem.* **20**, 229–236.

Fall, R., 1996: Cycling of methanol between plants, methylotrophs and the atmosphere, in M. E. Lidstrom and F. R. Tabita (eds), *Microbial Growth on C_1 Compounds*, Kluwer Academic Publishers, the Netherlands, pp. 343–350.

Fall, R. and Benson, A. A., 1996: Leaf methanol – the simplest natural product from plants, *Trends in Plant Science* **1**, 296–301.

Femenia, A., Garosi, P., Roberts, K., Waldron, K. W., Selvendran, R. R., and Robertson, J. A., 1998: Tissue-related changes in methyl-esterification of pectic polysaccharides in cauliflower (*Brassica oleracea* L. var. *botrytis*) stems, *Planta* **205**, 438–444.

Field, C. B., Behrenfeld, M. J., Randerson, J. T., and Falkowski, P., 1998: Primary production of the biosphere: integrating terrestrial and oceanic components, *Science* **281**, 237–240.

Finnegan, E. J., Genger, R. K., Peacock, W. J., and Deniss, E. S., 1998: DNA methylation in plants, *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **49**, 233–247.

Fisher, G. S., Legendre, M. G., Lovgren, N. V., Schuller, W. H., and Wells, J. A., 1979: Volatile constituents of southernpea seeds [*Vigna unguiculata* (L.) Walp.], *J. Agric. Food Chem.* **27**, 7–11.

Frenkel, C., Peters, J. S., Tieman, D. M., Tiznado, M. E., and Handa, A. K., 1998: Pectin methylesterase regulates methanol and ethanol accumulation in ripening tomato (*Lycopersicon esculentum*) fruit, *J. Biol. Chem.* **273**, 4293–4295.

Fry, S. C., 1988: *The Growing Plant Cell Wall: Chemical and Metabolic Analysis*, Longman Horton, Essex, U.K.

Fukui, Y. and Doskey, P. V., 1998: Air-surface exchange of nonmethane organic compounds at a grassland site: seasonal variations and stressed emissions, *J. Geophys. Res.* **103**, 13153–13168.

Galbally, I. E., Garland, J. A., and Wilson, M. G. A., 1979: Sulphur uptake from the atmosphere by forest and farmland, *Nature* **280**, 49—50.

Galbally, I. E. and Roy, C. R., 1980: Destruction of ozone at the earth's surface, *Quart. J. Roy. Meteorol. Soc.* **106**, 599–620.

Goldan, P. D., Kuster, W. C., and Fehsenfeld, F. C., 1995a: Hydrocarbon measurements in the southeastern United States: the rural oxidants in the southern environment (ROSE) program 1990, *J. Geophys. Res.* **100**, 25945–25963.

Goldan, P. D., Trainer, M., Kuster, W. C., Parrish, D. D., Carpenter, J., Roberts, J. M., Yee, J. E., and Fehsenfeld, F. C., 1995b: Measurements of hydrocarbons, oxygenated hydrocarbons, car-

bon monoxide, and nitrogen oxides in an urban basin in Colorado: implications for emission inventories, *J. Geophys. Res.* **100**, 22771–22783.

Goldan, P. D., Kuster, W. C., and Fehsenfeld, F. C., 1997: Nonmethane hydrocarbon measurements during the tropospheric OH photochemistry experiment, *J. Geophys. Res.* **102**, 6315–6324.

Goldberg, R., Prat, R., and Morvan, C., 1994: Structural features of water-soluble pectins from mung bean hypocotyls, *Carbohyd. Polymers* **23**, 203–210.

Gordon, A. H., Lomax, J. A., Dalgarno, K., and Chesson, A., 1985: Preparation and composition of mesophyll, epidermis and fibre cell walls from leaves of perennial ryegrass (*Lolium perenne*) and Italian ryegrass (*Lolium multiflorum*), *J. Sci. Food Agric.* **36**, 509–519.

Gout, E., Aubert, S., Bligny, R., Rébeillé, F., Nonomura, A. R., Benson, A. A., and Douce, R., 2000: Metabolism of methanol in plant cells. Carbon-13 nuclear magnetic resonance studies, *Plant Physiol.* **123**, 287–296.

Grant, G. T., Morris, E. R., Rees, D. A., Smith, P. J., and Thom, D., 1973: Biological interactions between polysaccharides and divalent cations: the egg-box model, *FEBS Lett.* **32**, 195–198.

Guenther, A. B., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P. C., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. R., 1995: A global model of natural volatile organic compound emissions, *J. Geophys. Res.* **100**, 8873–8892.

Haber, C. L., Allen, L. N., Zhao, S., and Hanson, R. S., 1983: Methylotrophic bacteria: biochemical diversity and genetics, *Science* **221**, 1147–1153.

Hayashi, T., Morikawa, H., Nakajima, N., Ichikawa, Y., and Senda, M., 1980: Oriented structure of pectic polysaccharides in pea epidermal cell walls, *Plant Cell Physiol.* **21**, 999–1005.

Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., and Zellner, R., 2000: CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry, *J. Atmos. Chem.* **36**, 231–284.

Higgins, J., Scott, D., and Hammond, R. C., 1984: Transformation of C_1 compounds by microorganisms, in D. T. Gibson (ed.), *Microbial Degradation of Organic Compounds*, Marcel Dekker, New York, pp. 43–87.

Holland, F., Aschmutat, U., Heßling, M., Hofzumahaus, A., and Ehhalt, D. H., 1998: Highly time resolved measurements of OH during POPCORN using laser induced fluorescence spectroscopy, *J. Atmos. Chem.* **31**, 205–225.

Holzinger, R., Warneke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., Schade, G., and Crutzen, P. J., 1999: Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile and hydrogen cyanide, *Geophys. Res. Lett.* **26**, 1161–1164.

Holzinger, R., Sandoval-Soto, L., Rottenberger, S., Crutzen, P. J., and Kesselmeier, J., 2000: Emissions of volatile organic compounds from *Quercus ilex* L. measured by Proton Transfer Reaction Mass Spectrometry under different environmental conditions, *J. Geophys. Res.* **105**, 20573–20579.

Houghton, R. A., Hackler, J. L., and Lawrence, K. T., 1999: The U.S. carbon budget: contributions from land-use change, *Science* **285**, 574–578.

Hugouvieux-Cotte-Pattat, N., Condemine, G., Nasser, W., and Reverchon, S., 1996: Regulation of pectinolysis in *Erwinia chrysanthemi*, *Annu. Rev. Microbiol.* **50**, 213–257.

Ishii, T., 1997: Structure and functions of feruloylated polysaccharides, *Plant Science* **127**, 111–127.

Jacob, D. J., Sillman, S., Logan, J. A., and Wofsy, S. C., 1989: Least dependent variables method for simulation of tropospheric ozone, *J. Geophys. Res.* **94**, 8497–8509.

Jarvis, M. C., 1984: Structure and properties of pectin gels in plant cell walls, *Plant Cell Environ.* **7**, 153–164.

Jarvis, M. C., Forsyth, W., and Duncan, H. J., 1988: A survey of the pectic content of nonlignified monocot cell walls, *Plant Physiol.* **88**, 309–314.

Kim, J.-B. and Carpita, N. C., 1992: Changes in esterification of the uronic acid groups of cell wall polysaccharides during elongation of maize coleoptiles, *Plant Physiol.* **98**, 646–653.

Kirk, T. K. and Farrell, R. L., 1987: Enzymatic 'combustion': the microbial degradation of lignin, *Annu. Rev. Microbiol.* **41**, 465–505.

Kirstine, W., Galbally, I. E., Ye, Y., and Hooper, M. A., 1998: Emissions of volatile organic compounds (primarily oxygenated species) from pasture, *J. Geophys. Res.* **103**, 10605–10620.

Kirstine, W. and Galbally, I. E., 1998: Biogenesis of methanol and its emission from flowering plants, *Proceedings of the 14th International Clean Air and Environment Conference*, Melbourne, Australia, pp. 517–522.

Kreuzwieser, J., Schnitzler, J.-P., and Steinbrecher, R., 1999: Biosynthesis of organic compounds emitted by plants, *Plant Biol.* **1**, 149–159.

Lamanna, M. S. and Goldstein, A. H., 1999: In situ measurements of C_2–C_{10} volatile organic compounds above a Sierra Nevada ponderosa pine plantation, *J. Geophys. Res.* **104**, 21247–21262.

Leibrock, E. and Slemr, J., 1997: Method for measurement of volatile oxygenated hydrocarbons in ambient air, *Atmos. Environ.* **31**, 3329–3339.

Lelieveld, J., Crutzen, P. J., and Rodhe, H., 1989: Zonal average cloud characteristics for global atmospheric chemistry modelling, GLOMAC report CM-76, UDC 551.510.4, International Meteorological Institute in Stockholm.

Lelieveld, J. and Crutzen, P. J., 1991: The role of clouds in tropospheric photochemistry, *J. Atmos. Chem.* **12**, 229–267.

Lide, D. R. (ed.), 1999: *CRC Handbook of Chemistry and Physics*, 80th edn, CRC Press, Boca Raton.

Liss, P. S. and Slater, P. G., 1974: Flux of gases across the air-sea interface, *Nature* **247**, 181–184.

Liss, P. S., 1983: Gas transfer: experiments and geochemical implications, in P. S. Liss and W. G. N. Slinn (eds), *Sea Exchange of Gases and Particles*, D. Reidel Publishing Co., Dordrecht, pp. 241–298.

MacDonald, R. C. and Fall, R., 1993: Detection of substantial emissions of methanol from plants to the atmosphere, *Atmos. Environ.* **27A**, 1709–1713.

Mangos, T. J. and Haas, M. J., 1997: A spectrophotometric assay for the enzymatic demethoxlyation of pectins and the determination of pectinesterase activity, *Anal. Biochem.* **244**, 357–366.

Margan, D. E., Graham, N. M., Minson, D. J., and Searle, T. W., 1988: Energy and protein values of four forages including a comparison between tropical and temperate species, *Aust. J. Exp. Agric.* **28**, 729–736.

Massiot, P., Perron, V., Baron, A., and Drilleau, J.-F., 1997: Release of methanol and depolymerization of highly esterified apple pectin with an endopolygalacturonase from *Aspergillus niger* and pectin methylesterases from *A. niger* or from orange, *Lebensm.-Wiss. u.-Technol.* **30**, 697–702.

McCann, M. C. and Roberts, K., 1991: Architecture of the primary cell wall, in C. W. Lloyd (ed.), *The Cytoskeletal Basis of Plant Growth and Form*, Academic Press, London, pp. 109–129.

McCann, M. C., Shi, J., Roberts, K., and Carpita, N. C., 1994: Changes in pectin structure and localization during the growth of unadapted and NaCl-adapted tobacco cells, *Plant J.* **5**, 773–785.

McFeeters, R. F. and Armstrong, S. A., 1984: Measurement of pectin methylation in plant cell walls, *Anal. Biochem.* **139**, 212–217.

McKenzie, L. M., Hao, W. M., Richards, G. N., and Ward, D. E., 1995: Measurement and modeling of air toxins from smouldering combustion of biomass, *Environ. Sci. Technol.* **29**, 2047–2054.

McNeil, M., Darvill, A. G., Fry, S. C., and Albersheim, P., 1984: Structure and function of the primary cell walls of plants, *Annu. Rev. Biochem.* **53**, 625–663.

Merk, S. and Riederer, M., 1997: Sorption of volatile C1 to C6 alkanols in plant cuticles, *J. Exp. Bot.* **48**, 1095–1104.

Miller, B. R., Huang, J., Weiss, R. F., Prinn, R. G., and Fraser, P. J., 1998: Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, *J. Geophys. Res.* **103**, 13237–13248.

Mopper, K. and Zhou, X., 1990: Hydroxyl radical photoproduction in the sea and its potential impact on marine processes, *Science* **250**, 661–664.

Monad, A. and Carlier, P., 1999: Impact of clouds on the tropospheric ozone budget: direct effect of multiphase photochemistry of soluble organic compounds, *Atmos. Environ.* **33**, 4431–4446.

Morris, E. R., Gidley, M. J., Murray, E. J., Powell, D. A., and Rees, D. A., 1980: Characterization of pectin gelation under conditions of low water activity, by circular dichroism, competitive inhibition and mechanical properties, *Int. J. Biol. Macromol.* **2**, 327–330.

Moustacas, A.-M., Nari, J., Borel, M., Noat, G., and Ricard, J., 1991: Pectin methylesterase, metal ions and plant wall extension: the role of metal ions in plant cell-wall extension, *Biochem. J.* **279**, 351–354.

Mudgett, M. B. and Clarke, S., 1993: Characterisation of plant L-isoaspartyl methyltransferases that may be involved in seed survival: purification, cloning, and sequence analysis of the wheat germ enzyme, *Biochemistry* **32**, 11100–11111.

Nari, J., Noat, G., and Ricard, J., 1991: Pectin methylesterase, metal ions and plant cell-wall extension, *Biochem. J.* **279**, 343–350.

Nemecek-Marshall, M., MacDonald, R. C., Franzen, J. J., Wojciechowski, C. L., and Fall, R., 1995: Methanol emission from leaves, *Plant Physiol.* **108**, 1359–1368.

Nursten, H. E., 1970: Volatile compounds: the aroma of fruits, in A. C. Hulme (ed.), *The Biochemistry of Fruits and Their Products*, Volume 1, Academic Press, New York, pp. 240–267.

Plass, C., Koppmann, R., and Rudolph, J., 1992: Light hydrocarbons in the surface water of the mid-Atlantic, *J. Atmos. Chem.* **15**, 235–251.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R. H. J., Porter, L., and Miller, B. R., 2001: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science* **292**, 1882–1888.

Reid, I. D., 1992: Demethylation of the lignin model dimer 1-(3′,4′-dimethoxyphenyl)-2-(o-methoxyphenoxy)-propane-1,3-diol by the white rot fungus *Phlebia tremellosa*, *Can. J. Bot.* **70**, 453–460.

Rexová-Benková, L. and Markovic, O., 1976: Pectic enzymes, *Adv. Carbohydr. Chem. Biochem.* **33**, 323–385.

Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kleindienst, T., Lonneman, W., Bertman, S., Shepson, P., and Starn, T., 1998: Observations of nonmethane hydrocarbons and oxygenated organic compounds at a rural site in the southeastern United States, *J. Geophys. Res.* **103**, 28111–28128.

Sanderson, M. (ed.), 1990: *UNESCO Sourcebook in Climatology*, UNESCO, France.

Schade, G. W. and Goldstein, A. H., 2001: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, *J. Geophys. Res.* **106**, 3111–3123.

Schlesinger, W. H., 1997: *Biogeography: an Analysis of Global Change*, 2nd edn, Academic Press, San Diego.

Seinfeld, J. H. and Pandis, S. M., 1998: *Atmospheric Chemistry and Physics*, Wiley Interscience, New York.

Singh, H. B., Kanakidou, M., Crutzen, P. J., and Jacob, D. J., 1995: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature* **378**, 50–54.

Singh, H., Chen, Y., Tabazadeh, A., Fukui, Y., Bey, I., Yantosca, R., Jacob, D., Arnold, F., Wohlfrom, K., Atlas, E., Flocke, F., Blake, D., Blake, N., Heikes, B., Snow, J., Talbot, R., Gregory, G., Sachse, G., Vay, S., and Kondo, Y., 2000: Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, *J. Geophys. Res.* **105**, 3795–3805.

Snider, J. R. and Dawson, G. A., 1985: Tropospheric light alcohols, carbonyls, and acetonitrile: concentrations in the southwestern United States and Henry's law data, *J. Geophys. Res.* **90**, 3797–3805.

Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., Foreman-Fowler, M., Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C.,

and McElroy, M. B., 2000: Three-dimensional climatological distribution of tropospheric OH: update and evaluation, *J. Geophys. Res.* **105**, 8931–8980.

Tyndall, G. S., Cox, R. A., Granier, C., Lesclaux, R., Moortgat, G. K., Pilling, M. J., Ravishankara, A. R., and Wallington, T. J., 2001: Atmospheric chemistry of small organic peroxy radicals, *J. Geophys. Res.* **106**, 12157–12182.

van Elsas, J. D., Trevors, J. T., and Wellington, E. M. H., 1997: *Modern Soil Microbiology*, Marcel Dekker, New York.

Vitousek, P. M., Ehrlich, P. R., Ehrlich, A. H., and Matson, P. A., 1986: Human appropriation of the products of photosynthesis, *BioScience* **36**, 368–373.

Vreeland, V., Morse, S. R., Robichaux, R. H., Miller, K. L., Hua, S.-S., and Laetsch, W. M., 1989: Pectate distribution and esterification in Dubautia leaves and soybean nodules, studied with a fluorescent hybridization probe, *Planta* **177**, 435–446.

Wang, K.-Y. and Shallcross, D. E., 2000: A Lagrangian study of the three-dimensional transport of boundary-layer tracers in an idealised baroclinic-wave-life-cycle, *J. Atmos. Chem.* **35**, 227–247.

Warneke, C., Karl, T., Judmaier, H., Hansel, A., Jordan, A., and Lindinger, W., 1999: Acetone, methanol, and other partially oxidized volatile organic emissions from dead plant matter by abiological processes: significance for atmospheric HO_x chemistry, *Global Biogeochem. Cycles* **13**, 9–17.

Yokelson, R. J., Goode, J. G., Ward, D. E., Susott, R. A., Babbitt, R. E., Wade, D. D., Bertschi, I., Griffith, D. W. T., and Hao, W. M., 1999: Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy, *J. Geophys. Res.* **104**, 30109–30125.

Zhou, X. and Mopper, K., 1990: Determination of photochemically produced hydroxyl radicals in seawater and freshwater, *Mar. Chem.* **30**, 71–88.