Atmospheric Methanol Budget and Ocean Implication

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Abstract: Methanol is a biogeochemically active compound and a significant component of the volatile organic carbon in the atmosphere. It influences background tropospheric photochemistry and may serve as a tracer for biogenic emissions. The mass of methanol in the atmospheric reservoir, the annual mass flux of methanol from sources to sinks, and the estimated atmospheric lifetime of methanol in the free troposphere, marine boundary layer, continental boundary layer, and in-cloud, are evaluated. The atmosphere contains approximately 4 Tg (terra-grams, 10^{12} g) of methanol. Estimates of global methanol sources and sinks total 340 and 270 Tg-methanol yr^{-1}, respectively, and are in balance given their estimated precision. Sink terms were evaluated using observed methanol distributions; the total loss is approximately a factor of 5 larger than prior estimates. The adopted source is a factor of 3 larger than its prior estimate. Recent net-flux observations and the magnitude of the estimated sink suggest biogenic methanol emissions to be near their current estimated upper limit, >280 Tg-methanol yr^{-1}, and this value was adopted. The methanol source will be larger with the inclusion of an argued for oceanic gross emission of 30 Tg-methanol yr^{-1}, but a major uncertainty concerns whether the oceans are a major net sink or source of methanol, an issue which will not be resolved without new measurements. Other large uncertainties are the estimates of primary biogenic emissions and gas surface deposition. The first loss estimates of methanol by in-cloud chemistry and precipitation are presented. They are approximately equal at 10 Tg-methanol yr^{-1}, each. These are small in comparison to the surface loss and gas phase photochemical loss estimated here but would be significant additional losses in earlier budgets. Surface exchange processes dominate the atmospheric budget of methanol and its distribution. The atmospheric deposition of methanol and the argued for methanol produced in the upper ocean are ubiquitous sources of C_1 substrate capable of sustaining methylotrophic organisms throughout the surface ocean.

1. Introduction

Methanol is the predominant oxygenated organic compound in the background mid to upper troposphere (*Singh et al.*, 2000, 2001). Methanol emissions represent approximately 6% of identified terrestrial biogenic organic carbon sources to the atmosphere based upon the data in *Fall* [1999] and this work (Table 1). For comparison, global methanol sources, on a carbon mass basis, may be a factor of 2 larger than those inferred by *Jacob et al.* [2002] for acetone. The atmospheric lifetime of methanol due to the reaction with gaseous HO alone is on the order of 19 days, based on observed methanol distributions and predicted HO fields from the global photochemical model of *Bey et al*. [2001]. Consequently, methanol is transported globally (e.g., *Singh et al.*, 2001) and is proposed to have a role in tropospheric oxidant photochemistry (e.g., *Fehsenfeld et al.*, 1992; *Kelly et al.*, 1994; *Monod et al.*, 2000). Additionally, methanol could serve as an intermediate-lived atmospheric tracer of terrestrial biogenic emissions, as it is emitted from a variety of plant species (*Fall and Benson*, 1996), although its efficacy as a tracer would be reduced should oceanic emissions prove to be significant.

Methanol directly reacts with hydroxyl radicals (HO) in gas and aqueous phases. The reaction products are a subsequent source of formaldehyde, hydrogen radicals, and ozone. In addition, methanol photochemistry in cloud water can be a source of formic acid (e.g., *Jacob* 1986, 2000); and it therefore has a potential role in establishing the background acidity of cloud and rainwater. In-cloud methanol chemistry confounds the prediction of cloud effects on, for example, atmospheric ozone, formaldehyde, carbon monoxide, and molecular hydrogen (*Lelieveld and Crutzen*, 1991; *Jacob*, 2000; *Monod et al*., 2000). The methanol photochemical lifetime is long compared to formaldehyde (~1 day), and methylhydroperoxide (1-2 days); the predominant oxygenated organic compounds in the lower troposphere especially over continents. Methanol lifetime in the surface boundary layer is 3-6 days and in cloud it is 9 days. Quantification of methanol distributions, the global sinks of methanol, and its global sources is needed before the significance of methanol on tropospheric photochemistry can be accurately determined.

Measurements of methanol in the near surface atmosphere, though limited in number, show a consistent range of values within general land use types (Table 2). Most of the data are from spring-summer measurement campaigns during vegetative growth stages and seasonal information from single locales is sparse. Typical methanol surface concentrations are estimated at 900 pptv (pptv is defined as 10^{12} times the molecular mixing ratio of methanol in air) over the remote ocean, 2000 pptv for continental background, 6000 pptv for grasslands, 10000 pptv for coniferous and deciduous forests, and >20000 pptv for urban areas. *Kelly et al*. [1993] report three extreme observations (78500, 212000, and 297000 pptv) in a wooded North Carolina industrial area. Isolated methanol observations in the Arctic have been reported during summer by *Cavanagh et al.* [1969] and during polar sunrise by *Boudries et al.* [2002] with mean values nominally 800 and 250 pptv, respectively. The mean methanol concentration for four Arizona rainwater samples from *Snider and Dawson* [1985] is also listed – the only rainwater

observations available. Estimates of methanol concentrations in atmospheric water are also given assuming gas-aqueous thermodynamic equilibrium, Henrys' Law data from Snider and *Dawson* [1985], and the typical gas concentrations stated above. Atmospheric water concentrations are predicted to range from 0.2 to >$4x10^{-6}$ M for 25°C, or from 0.9 to >$20x10^{-6}$ M for 0°C along a gradient from background ocean to urban conditions.

Methanol observations aloft are few. *Singh et al*. [1995; 2000; 2001] have reported values for the remote atmosphere over the Atlantic and Pacific from 0.3 to 12 km. Mixing ratios between 200 and 1000 pptv were shown and 600 pptv is estimated as a central value for the free troposphere (FT). *Doskey and Gao* [1999] showed lower tropospheric methanol observations near the top of the boundary layer over Harvard Forest, MA, and these ranged from 5000-15000 pptv and were approximately ½ those measured near the surface. Mountain site data from Colorado suggest background concentrations of 2000 pptv (*Goldan et al*., 1997) in the lower continental troposphere. Karl (T. Karl, personal communication) has data from a Colorado mountain site showing similar values. He also has data, which range from 500-2000 pptv for Mauna Loa Observatory (MLO), HI. MLO is at approx. 3 km altitude, is subject to strong upslope-downslope flow, and mixing ratios there reflect at times lower FT air, island modified MBL air, or a mixture of these air mass types. *Williams et al*. [2001] reported methanol from the initial airborne deployment of a proton transfer reaction mass spectrometer. Their measurements were in the tropics over Surinam during March and mean FT(>3km) and lower-FT (<3km) mixing ratios were 600 and 1100 ppt, respectively. The latter value is low compared with other mid-latitude continental observations.

The present atmospheric budget of methanol is poorly constrained (*Singh et al*., 2000; 2001) and is the subject of this work. *Singh et al*. [2000] estimated the total atmospheric methanol source at 122 Tg yr^{-1} with fossil-fuel combustion (3 Tg-methanol yr^{-1}), terrestrial primary biogenic emissions (75 Tg-methanol yr^{-1}), methane oxidation (18 Tg-methanol yr^{-1}), terrestrial biomass decay (20 Tg-methanol yr^{-1}), and biomass burning (6 Tg-methanol yr^{-1}) considered separately. An oceanic source was suggested but without a value given. Their combined sources exceeded the sum of the two methanol sinks considered, 40-50 Tg-methanol yr^{-1}, by a factor of 2 to 3. This discrepancy motivated a more critical examination of other methanol sinks (section 2) including precipitation removal and in-cloud chemistry, as well as, a reassessment of losses by surface gas deposition and HO reaction. We used observed mixing ratios to estimate loss rates in our analysis and found our new combined sink exceeded their source estimate by about 2.5. The newfound excess in global loss prompted a reconsideration of sources (section 3) principally the primary terrestrial biogenic source with the inclusion of recent net-flux studies (section 4) and an evaluation of a possible oceanic source. Table 3 summarizes the data used to establish the primary terrestrial biogenic source of methanol. Table 4 presents a revised budget for atmospheric methanol based on this effort. The budget is presented in units of Tg-methanol (terra-grams of methanol) for consistency with the earlier Singh et al. budget. Table 4 includes a hypothesized but untested oceanic source of methanol. Table 5 summarizes phytoplankton culture work in support of this hypothesis. While

this work strives to develop methanol budget closure, it calls out the uncertainty in global source and sink terms.

2. Methanol Sinks Considered

There are no studies quantifying methanol loss on a global basis aside from that of *Singh et al*. [2000], wherein they considered two methanol sink processes: gas phase hydroxyl radical (HO) reaction and surface deposition (uniform global deposition velocity, V_s, of 0.1 cm s^{-1}). These and other methanol loss processes including consumption by leaf microbes, precipitation, dew, and atmospheric vertical transport and mixing, have been identified to explain daily cycles and rapid changes in methanol concentrations observed in surface time-series (e.g., *Snider and Dawson* 1985; *Goldan et al*., 1995a,b, 1997; *Fall*, 1996; *Leibrock and Slemr*, 1997; *Doskey and Gao*, 1999, *Riemer et al*., 1998). An in-cloud loss by the aqueous reaction of methanol with HO can be added to this list based on the work of *Jacob* [1986], *Lelieveld and Crutzen* [1991], and *Monod and Carlier* [1999]. The following is an initial global analysis of methanol loss by aqueous methanol-HO reaction in cloud and precipitation deposition to land and ocean. These are followed by re-analyses of its losses through "dry" deposition to land and ocean and methanol-HO reaction in the gas phase. Such estimates have necessarily large variances and these are included in Table 4. The sink terms are evaluated using observed atmospheric mixing ratios.

2.1. Aqueous Phase HO Reaction

Methanol loss by reaction with HO can occur in the gas phase and in the aqueous phase within atmospheric water (e.g., haze aerosol, clouds, fog, rain). In cloud aqueous reactions of methanol have been discussed as they pertain to HO, formaldehyde, and ozone chemistry (e.g., *Monod and Carlier*, 1999; *Jacob*, 2000; *Monod et al.*, 2001), but not as a sink of methanol. A simple calculation illustrates the potential for loss of methanol by aqueous HO chemistry in oceanic and continental water clouds. The overall aqueous reaction is:

$$HO + CH_3OH \rightarrow\rightarrow + O_2 \rightarrow\rightarrow CH_2O + H_2O + HO_2$$

The reaction rate constant is $1x10^9$ $M^{-1}s^{-1}$ and estimated from *Monod and Carlier* [1999]. A HO value of $0.1x10^{-12}$ M was used to estimate a minimum cloud loss rate based on *Jacob* [1986; 2000]. Gas-aqueous thermodynamic equilibrium is assumed to estimate maximum aqueous HO and to estimate methanol concentrations from their gas phase concentrations. For maximum HO, the global mean HO concentration of $1x10^6$ molecules cm^{-3} (*Prinn et al*., 1995) is used. This must be reduced by about 50% to account for in-cloud photochemical conditions (Jacob, 2000). The HO Henry's Law constant is 100 M atm^{-1} (T_{cloud} = 0°C, *Jacob*, 2000). This is reduced by 80% to account for kinetic gas-to-droplet mass-transfer limitations (*Jacob*, 1986), as HO reacts with many dissolved species in cloud water such that gas-droplet mass transfer of HO is unable to sustain aqueous concentrations near the thermodynamic equilibrium value. *Jacob* [1986] modeled in-cloud aqueous and gas phase HO concentrations as a function of droplet pH at 293ºK and the aqueous-to-gas ratio at pH = 5 was 4 M atm^{-1} which is about 20% of that expected from thermodynamic

equilibrium. The resultant maximum aqueous HO concentration is then 0.4×10^{-12} M. A background gas phase methanol concentration of 900 pptv (Table 2) was used for oceanic clouds and 2000 pptv (Table 2) was used for continental clouds. The methanol Henry's Law constant is 1000 M atm^{-1} (T_{cloud} = 0°C, *Snider and Dawson*, 1985). Resulting aqueous methanol concentrations are 2×10^{-6} M and 9×10^{-7} M for continental and oceanic clouds, respectively. The oceanic and continental cloud liquid water content was set to 3×10^{-7} L/L based upon values given by *Lelieveld and Crutzen* [1991]. Cloud volumes were estimated by multiplying fractional cloud sky cover times cloud thickness times oceanic and continental area. Low cloud cover over the ocean was taken to be 50% (*Warren et al*., 1988) with a cloud thickness defined to be 500 m (*Warneck*, 1999). Low cloud cover over the continents was taken to be 30% (*Warren et al*., 1986) with a cloud thickness defined to be 1000 m (*Warneck*, 1999). Only low clouds with liquid water have been considered. The tropospheric cloud volume estimated here is similar to the *Liang and Jacob* [1997] estimate of 10%, which compared well with satellite derived column liquid water contents. The resulting global aqueous loss estimate for methanol via HO reaction in cloud is 10 Tg-methanol yr^{-1} and listed in Table 4. A loss of 10 Tg-methanol yr^{-1} represents an additional loss equal to 25% of the total loss estimated by *Singh et al.* [2000] but is less than 5% of the total loss estimated here. The relative uncertainties in global cloud volume, water content, aqueous [HO], aqueous [CH_3OH], and rate constant are estimated at 30% for each and results in approximately a factor of 2 uncertainty in the aqueous HO-methanol chemical sink.

Methanol loss on aerosols is not considered here. *Iraci et al*. [2002] examined methanol uptake by sulfuric acid aerosols and, while the solubility of methanol is dramatically enhanced at the sulfuric acid concentrations (40-75% by weight) and temperatures (197-241ºK) considered and aqueous rates of reaction in these aerosols are also enhance, they concluded sulfuric acid aerosols have a negligible impact on atmospheric aerosol because of the small aerosol liquid volume involved. We believe this will be the case for other aerosol compositions.

2.2. Ocean and Land Precipitation Deposition

"Wet" deposition losses are estimated to be 10 Tg-methanol yr^{-1} and this is also equal to 25% of the total estimated by *Singh et al.* [2000] and <5% of the methanol loss estimated here. Wet deposition was calculated by assuming thermodynamic equilibrium between the gas phase and precipitation water. *Snider and Dawson* [1985] have reported the sole measurement of methanol in precipitation. Their atmospheric gas phase measurement of 2600 pptv, rain measurement of 690 nM, and Henry's Law measurements show the system was near thermodynamic equilibrium. This suggests the equilibrium assumption to be a reasonable approximation. Precipitation rates for land and ocean were taken from *Peixoto and Oort* [1992] and convolved with the background oceanic and continental values of Table 2 to estimate the wet deposition to land, 5 Tg-methanol yr^{-1}, and to the ocean, 5 Tg-methanol yr^{-1}. These are listed in Table 4. The range is evaluated from variances in concentration, Henry's Law constant (temperature) and precipitation estimates.

2.3. Gas Phase HO Reaction

A similar calculation was performed to estimate the gas phase loss of methanol by reaction with HO. A three-box model of the atmosphere was applied. The lowest 2 km of the troposphere was considered in two parts, one oceanic with a methanol concentration of 900 pptv and the other continental with a concentration of 2000 pptv. A third box represented the global free troposphere with a methanol concentration of 600 pptv. HO was assumed constant for all three boxes at a concentration of $1x10^6$ molecules cm^{-3} in keeping with the global mean annual tropospheric estimate of *Prinn et al*. [1995]. The gas phase methanol-HO reaction rate constant was taken to be $8x10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. The resulting gas phase photochemical loss of methanol is 100 Tg-methanol yr^{-1}, about 37 % of its loss, and listed in Table 4. This value is about 2.5 times that estimated by *Singh et al*. [2000] for the same process. It is nearly identical to those estimated using global HO fields from the model of *Bey et al*. [2001] for January, 101 Tg-methanol yr^{-1}, and July, 105 Tg-methanol yr^{-1}. We have adopted a loss rate of 100 Tg-methanol yr^{-1} and acknowledge that the variability in methanol HO loss is large.

2.4. Ocean and Land "Dry" Deposition

Surface deposition can occur through "dry" and "wet" processes to land and ocean. A typical means of estimating the air-to-surface flux is through the concept of the deposition velocity, V_s, (e.g., *Wesely and Hicks*, 2000) which assumes the flux is proportional to the bulk air-surface concentration gradient and a transfer coefficient with units of velocity. *Singh et al.* [2000] assumed a V_s of 0.1 cm s^{-1} to estimate methanol deposition loss to land and ocean surfaces. We have reevaluated the surface dry depositional loss of methanol to the ocean and to land using the *Wesely* [1989] resistance model to estimate V_s for various land types and seasons and for the V_s to the ocean (*Duce et al.*, 1991). In this scheme aerodynamic, chemical-physical properties, material surface, and chemical reactivity considerations are treated as a series of resistances. For methanol, an oceanic V_s of 0.4 cm s^{-1} is expected at a wind speed of 5 m s^{-1} and V_s would increase to 1.1 cm s^{-1} for 10 m s^{-1} winds. On land, peak V_s is 0.9 cm s^{-1} for summer forest conditions under full sun and 0.04 at night. V_s's estimated for other vegetation types, times of day, and seasons lie within these values. *Wesely and Hicks* [2000] have reviewed measured V_s's for low molecular weight organic peroxides and organic acids and report V_s's of 0.5-1.1cm s^{-1} for formic acid. Organic peroxide surface resistances of 0.1-15 s cm^{-1} were listed implying V_s's of ~0.06-10 cm s^{-1}. A value of 10 cm s^{-1} is extreme. Methanol should behave similarly to organic peroxides based upon physical properties and biological reactivity. The continental V_s is set to 0.4 cm s^{-1}. The "typical" atmospheric surface concentrations from Table 2 were combined with the V_s estimates to calculate the "dry" deposition loss of methanol to land and ocean and these are listed in Table 4. Ranges were estimated by assigning a factor of two uncertainty on V_s and noted ranges in concentration. The global total "dry" depositional loss is estimated at 150 Tg-methanol yr^{-1}.

2.5 Total Loss Estimate

The total global annual loss of methanol from the atmosphere is 270 Tg-methanol. This is approximately a factor of 5 larger than that estimated earlier. It is also about 2-3 times the earlier source estimate. The lower-range loss estimate is also 50% in excess of the earlier source value. Hence, our analysis of losses shifts the methanol budget from being a factor of 2 heavy in sources to being a factor of 2 heavy in sinks.

3. Methanol Sources Reconsidered

The magnitude of the above total estimated methanol sink necessitated a reconsideration of global methanol sources. Emissions from fossil fuel combustion, biomass burning, and plant decay vary slightly from those estimated by *Singh et al*. [2000]. We have estimated fossil fuel emissions based upon the relationship between methanol and total reactive odd nitrogen (NO_y) noted by *Goldan et al.* [1995a]. The emissions from biomass burning were estimated using the average methanol-CO (carbon monoxide) ratio reported by *Yokelson et al*. [1998] and *Goode et al*. [2000] from their reviews of the literature. Fossil fuel nitrogen oxide emissions and biomass burning CO were taken from their respective global budget estimates in *Brasseur et al*. [1999]. The methanol source from plant matter decay is taken from *Warneke et al*. [1999]. The model of *Bey et al*. [2001] was used to evaluate photochemical methanol production in the atmosphere. Methanol source rates from these four processes are listed in Table 4. The range estimates are from propagating stated parameter variances. Methanol emissions from primary biogenic and oceanic sources exhibit the greatest uncertainty and are considered separately below.

3.1. Primary Biogenic Source Uncertainty

Guenther et al. [1995] formulated a global emission inventory of biogenic volatile organic carbon, VOC, and as a part of that effort assigned a single emission factor to be applied to a VOC category that included methanol and a variety of other VOCs with poorly understood emission processes. The total global emission of this other VOC category was estimated to be 260 Tg-carbon yr^{-1}. In that analysis, using very limited information from laboratory measurements of methanol emission from leaves (e.g., *MacDonald and Fall*, 1993), the primary biogenic source of methanol, was suggested to be in the range of >100 Tg-carbon yr^{-1} (a value of 280 Tg-methanol yr^{-1} is used here). Since the *Guenther et al*. [1995] model calculates a global emission of 260 Tg-carbon yr^{-1} for methanol and other VOC using an emission factor of 1.5 µg C g^{-1} h^{-1}, a global methanol emission of 100 Tg-carbon yr^{-1} would require an average methanol emission factor of 0.57 µg C g^{-1} h^{-1}, which represents >0.2% of global terrestrial primary production.

Subsequently, several investigators have measured methanol emissions from vegetation in both laboratory and field settings, and this data is summarized in Table 3. Several brief generalizations can be made from laboratory investigations: 1) young, rapidly dividing leaves show the greatest emission rate; 2) emissions in undisturbed leaves are highest when transpiration is highest; 3) methanol emissions from conifers are lower than from broad-leaf plants, and 4) methanol releases are greatly enhanced by leaf wounding (*MacDonald and Fall*, 1993; *Nemecek-*

Marshall et al., 1995). Mean methanol fluxes ranging from 0.5-31 µg C g^{-1} h^{-1} were obtained with a variety of plants. Most of these values are much higher than the conservative value of 1.5 µg C g^{-1} h^{-1} used by *Guenther et al*. [1995] for methanol plus other VOC. However, *Holzinger et al*. [2000] have reported a laboratory study with Mediterranean holm oak, which shows a much lower flux of about 0.5 µg C g^{-1} h^{-1}, illustrating the need for further careful measurements of methanol emission factors in a variety of plants. These results also point out the difficulty in assigning a global methanol emission factor, since leaf emissions are so dependent on leaf age and stomatal transpiration, factors that vary considerably during the growing season.

A variety of field measurements generally support the assumptions used by *Guenther et al*. [1995] to derive their methanol emission estimate, and this information is also shown in Table 3. For example, *Kirstine et al*. [1998] and *Fukui and Doskey* [1998] examined VOC release in grasses or grassland and found methanol emission rates in the range of 0.5 to 20 mg m^{-2} h^{-1}, with higher emissions in disturbed vegetation, consistent with laboratory findings that methanol pools exist in leaves and are released upon wounding. A variety of other field measurements (*Baker et al*., 2001; *Schade and Goldstein*, 2001; *Karl et al*., 2001; *Warneke et al*., 2002; *Geron et al*.; 2002) in many different ecosystems give methanol fluxes (growing season) in the range of 0.5-4 mg m^{-2} h^{-1} (Table 3). When expressed on a leaf dry weight basis these values generally argue for a methanol emission factor higher than that estimated by *Guenther et al*. [1995]. It is noteworthy that the *Guenther et al*. [1995] emission factor for VOC is dependent only on temperature. If we estimate global methanol emissions using the algorithm that *Guenther et al.* [1995] used for isoprene, which assumes that emissions are reduced in the dark, and assume that methanol emissions are greatly reduced for older leaves, then we would need a methanol emission factor, for young leaves exposed to sunlight, of about 4 µg C g^{-1} h^{-1} in order to get the same global emission rate. However, given the lack of methanol flux measurements in different ecosystems over the growing season, retaining the conservative emission factor seems justified.

The above consideration of loss processes, totaling 270 Tg-methanol yr^{-1} also argues for a larger vegetative methanol source closer to *Guenther et al*. In Table 4, the primary biogenic source minimum and maximum are that of *Singh et al*. [2000] and *Guenther et al*. [1995], respectively. This source is for terrestrial vegetation emissions alone.

3.2. Ocean Source

Methanol input to the atmosphere would be higher with the inclusion of a hypothesized but unquantified oceanic source (*Singh et al*., 2000). An oceanic source of methanol is inferred from photochemical modeling studies of the remote MBL (Chang, 2002) and discussed in section 3.2.1. The ocean source needed to satisfy the model and atmospheric observations is estimated at 30 Tg-methanol yr^{-1} with a range estimate of 0-80 Tg-methanol yr^{-1}. The limits are heuristic. The lower value stems from an assumption that methanol is readily dissolved in seawater and consumed rapidly by bacteria and other organisms. The upper limit derives from the maximum flux needed to

maintain observed MBL methanol mixing ratios over the subtropical remote ocean for a case without FT-MBL material exchange.

The likelihood of a global oceanic methanol source equal to 30 Tg-methanol yr^{-1} is difficult to evaluate. Observations of methanol in seawater have not been reported. *In situ* oceanic methanol sources are speculative, principally biological, and expected to be temporally and spatially inhomogeneous. *Sieburth* [1988] and *Sieburth and Keller* [1989] indicated that bacterial consortia are able to ferment algal carbohydrates to methanol within the aerobic upper ocean. Further support of oceanic biological methanol formation comes from Riemer (unpublished data, 1998), who observed methanol in the headspace gas of laboratory phytoplankton cultures (Table 5), an example of culture data is shown in Figure 1. Assuming a Henry's Law constant of 200 M atm^{-1} (appropriate to fresh water at T=25ºC), the observed methanol mixing ratios suggest culture seawater methanol concentrations $>1x10^{-6}$ M. This concentration is close to that reported by King et al. [1983] for *in situ* sediment water from a Maine tidal anoxic sediment, $2x10^{-6}$ M. While Riemer's experiments were focused upon the determination of isoprene production (Milne et al., 1995), the methanol observations imply its production within the cultures. Methanol was observed with all cultures during exponential and stationary phase growth. Since marine phytoplankton are the most abundant organisms on Earth and their primary production is equal to terrestrial primary production, even production of small amounts of methanol would be a very significant global source.

Oceanic methanol sink processes should also be considered in an assessment of ocean methanol. Briefly, these include photochemical loss and microbial uptake. Again studies of methanol consumption in seawater have not been reported. Methanol does not readily photolyze in air or seawater. It is relatively unreactive with hydrated electrons, superoxide or perhydroxyl. It does react with HO in water and a simple methanol HO-lifetime estimate is ≥40 days, where $\tau_{HO}=1/k/[HO]_{sw}$, the seawater $[HO]_{sw}$ concentration is $<3x10^{-16}$ M (*Mopper and Zhou*, 1990), and $k=1x10^{9}$ $M^{-1}s^{-1}$ as above. Thus, methanol is long lived with respect to photochemical oxidation. *Kiene* [1993] suggested methanol as a carbon and energy source for oceanic methylotrophic organisms (these bacteria are often cultured in a medium containing methanol) and stated little was known about methanol's biogeochemical cycling. A rate for oceanic bacterial methanol uptake is not known but we estimate it has a 3 day lifetime based on experimental biological turnover times for DMSP (dimethylsulfoniopropionate) (*Simo et al*., 2000), methylamines (*Yang et al*., 1994), and formaldehyde (*Mopper and Kieber*, 1991), and inferred GBT (glycine betaine) turnover times (*Kiene and Hoffmann-Williams*, 1998; *Gibb et al*., 1999).

For comparison, atmospheric acetone, like methanol, also has an implied ocean emission. *Jacob et al*. [2002] inferred an oceanic source of acetone of 17 Tg-carbon yr^{-1} using a global photochemical inverse model calculation. The model included acetone deposition to the oceans and a net flux out of the ocean was predicted. On a grams of carbon basis, our inferred methanol oceanic source is ~2/3's of their acetone source, but our calculations (Table 4) suggest the ocean is a net methanol sink.

Several possible methanol formation schemes are briefly outlined below involving biological processes or chemistry. The emphasis is placed on identifying which of these speculative processes are capable of methanol production at the rate implied by the MBL modeling study.

3.2.1. Air-to-Sea Transport

Atmospheric measurements of methanol in the remote marine boundary layer (MBL) show concentrations of about 900 pptv on average with slightly lower concentrations, approx. 600 pptv, in the free troposphere (FT) (*Singh et al*., 2000; 2001). A one-dimensional model of MBL methanol photochemistry with seawater methanol concentrations set to 0 showed methanol to deplete in the tropical-subtropical MBL with about a 3-day lifetime due to surface deposition (Chang, 2002). It was not possible for this model to predict observed remote MBL methanol levels. Inclusion of photochemical methanol production alone led to predicted mixing ratios <120 pptv. The addition of FT-to-MBL transport raised the calculated methanol mixing ratio to 450 pptv and 700 pptv when FT mixing ratios were assumed to be 900 and 1800 pptv, respectively. The latter is a high estimate from *Singh et al*. [2001]. Oceanic methanol emissions were required for the model to sustain methanol mixing ratios at the observed MBL level (900 pptv). In the case of photochemistry alone, gross oceanic emissions were required to be nearly equal to the gross rate of surface depositional loss, thereby, reducing the net methanol flux to near zero. For this case, a net zero flux implied an oceanic source of 80 Tg yr^{-1} and implied an oceanic surface film concentration between 0.2 and 2.0×10^{-6} M depending upon temperature. This is the maximum emission listed in Table 4. In the case where FT to MBL exchange is included, gross oceanic emission rates of ¼ to ½ those of the gross surface deposition, 20-40 Tg-methanol yr^{-1}, were required and this implies a surface concentration of 0.05-0.5×10^{-6} M. This case was used to define the nominal ocean emission rate of 30 Tg-methanol yr^{-1} and serves as the target value for the oceanic sources described below.

3.2.2. Methyl Halide Hydrolysis

Zafiriou [1975] and *Elliot and Rowland* [1995] proposed that methanol could be produced by the hydrolysis of methyl halides emitted by phytoplankton. The global methanol production rate from methyl halides hydrolysis is quite small and totals less than 0.3 Tg-methanol yr^{-1} based on the work of *Moore et al.* [1996] for methyl chloride, *Anbar et al.* [1996] for methyl bromide, and *Moore and Groszko* [1999] for methyl iodide. This process is unimportant to atmospheric methanol.

3.2.3. Methane Oxidation

Fugitive emissions from methanogenic and methanotrophic organisms in the upper water column (e.g., *Sieburth et al*., 1987; *Sieburth and Keller*, 1989; *Kiene*, 1993), could result in seawater methanol due to inefficiencies in the methane-methanol-formaldehyde-formate biochemical coupling. However, such inefficiencies are unlikely given the fact methanol is a key intermediate in yielding energy from methane oxidation. Regardless, an upper limit for this source can be estimated for the upper ocean (Our focus is on atmospheric methanol and we have restricted the discussion to the upper ocean and have ignored methane oxidation at depth where sediment emissions from methanogens or hydrate dissociation can be significant and methane oxidation rates high). *Cicerone and Oremland* [1988]

and *Holmes et al*. [2000] have estimated upper ocean methane production at 5-20 Tg-carbon yr^{-1}. *Holmes et al*. [2000] estimated that less than 2% of the methane produced in the upper oligotrophic North Atlantic and North Pacific is oxidized there. While the fraction of methane oxidized in the upper ocean appears to increase with increasing nutrients towards the coast and in estuaries (e.g., *Ward et al*., 1987; 1989; *Jones*, 1991; *Bange et al.*, 1994; *Tsurushima et al.*, 1996; *Sansone et al.*, 1998; *Holmes et al*., 2000; *Jayakumar et al.*, 2001) and methane oxidation turnover time decreases sharply with methane concentration above 15 nM to lifetimes <5 yr (e.g.,*Valentine et al*., 2001), nearly all upper ocean methane appears to be simply lost to the atmosphere. If the ~2% of the oxidized methane (*Holmes et al*., 2000) went directly to methanol and all of this went into the atmosphere, the maximum oceanic methane-to-methanol production rate would be <0.53 Tg-methanol yr^{-1}. This is a vanishingly small source of atmospheric methanol.

3.2.4. Methylation/Demethylation Biochemical Cycles

The presence of carboxymethyl groups is well documented in the proteins and polysaccharides of living organisms. The hydrolysis of these methyl esters by acid- or base-catalyzed reactions, or by methylesterase enzymes results in the formation of methanol.

For example, the methanol source in vegetation (section 3.1) is thought to be primarily plant cell wall pectin, a polysaccharide rich in methyl ester linkages, that are enzymatically hydrolyzed, releasing methanol during cell wall expansion (*Fall and Benson*, 1996). In marine systems, however, pectin is not common in the cell walls of phytoplankton and seaweeds, which contain other types of polysaccharides, such as alginates, mannans, xylans, and sulfated polysaccharides, in addition to cellulose (*www.biologie.uni-hamburg.de/b-online/e26/26d.htm*). Only the sulfated polysaccharides contain significant amounts of methyl groups, where the methyl groups are linked by very stable ether linkages. It is notable that this type of methylated polysaccharide is reported to occur in most marine algae (*Painter*, 1983). If the turnover of such residues in the food chain results in demethylation to form methanol, as in lignin degradation by fungi (*Fall and Benson*, 1996), this might be a potentially large source of marine methanol, given the abundance of marine phytoplankton and their consumption in the food web.

It is tempting to think that some fraction of the abundant methylated osmoprotectants in marine organisms might be a methanol source. These protectants are characterized as highly methylated quaternary amino or tertiary sulfonium groups. For example, the annual turnover of the osmolyte, DMSP, in phytoplankton gives rise to oceanic emissions of 15-33 Tg S as CH_3SCH_3 (*Simo et al*., 2000). In addition, *Visscher and Taylor* [1994], *Simo et al*. [2000], and *Kiene et al*. [2000] have described bacteria utilizing DMSP as a source of carbon and energy. Although these types of bacteria are generally methanol consumers (methylotrophs), *Kiene et al*. [2000] estimated ocean DMSP utilization yields $3\text{-}90 \times 10^{-9}$ M d^{-1} of unspecified methylated compounds and CO_2. Assuming: 1) 1% of the total methylated material is released as methanol, 2) it is produced uniformly in the top 10 m of the ocean, and 3) it is delivered to the atmosphere then, the global methanol production rate would be 2-54 Tg yr^{-1}. *Simo et al*. [2000] observed a 3-day turnover time for DMSP and a similar methanol production estimate of 2-

20 Tg yr^{-1} is calculated using their turnover time and assuming surface DMSP concentrations of 10^{-8}-10^{-7} M, a 10 m thickness, and 1% methanol yield. DMSP consumption by bacteria is of the right order of magnitude to that needed. Compensating variations in DMSP concentration, yield, and surface ocean thickness would maintain this rate. For example, increasing the yield to 10% and decreasing the thickness to 1 m gives the same rate of methanol production.

Similar speculative estimates of the fate of another important marine osmolyte, GBT, might also support a significant methanol source. As with DMSP, GBT-degrading bacteria are able to demethylate GBT [*Sieburth and Keller*, 1989]. Seawater GBT concentrations are unknown but estimated to be on the order of 1-10x10^{-9} M (*Kiene et al.*, 1998; *Kiene and Hoffmann-Williaims*, 1998). *Kiene and Hoffmann-Williams* [1998] studied GBT biodegradation, and could account for only 41-91% of the GBT in their degradation experiments, and suggested the missing fraction went into soluble and volatile products. *Kiene et al*. [1998] argued that the biogeochemical cycling and turnover of GBT would be comparable to the turnover of DMSP. It remains to be determined if methanol is a product of GBT turnover. Other marine sources of methanol, could include methanol arising from protein repair pathways (*Kagan et al*., 1997) or as a result of protein demethylation during chemotaxis (*Grebe and Strock*, 1998), but the magnitude of such methanol production is uncertain. Finally, it should be noted that little is known of the metabolites arising from other levels of the marine food web. As a large amount of carbon is processed annually in this food web, it is probable that unknown marine methanol sources exist.

3.2.5. Other Marine C1 Observations

Formaldehyde and formate are subject to photochemical and biological formation and loss and have been measured in seawater. Formaldehyde ranges from 4-16x10^{-9} M for the open ocean and 10-40x10^{-9} M for coastal waters (*Mopper and Stahovec*, 1986; *Kieber and Mopper*, 1990; and *Zhou and Mopper*, 1997). Surface micro-layer concentrations in these systems are approximately a factor of 10 higher, ranging from 35x10^{-9} M to 45-170x10^{-9} M, respectively (*Zhou and Mopper*, 1997). *Zhou and Mopper* also determined formaldehyde in air near the ocean surface and concluded the ocean-atmosphere were near equilibrium such that at specific times and locations the ocean could be a source of formaldehyde, a compound with an effective solubility constant 10 times that of methanol. One of the arguments expressed against the idea of an oceanic source of methanol is its "large" solubility in water, an argument which would not hold up in the case of formaldehyde. Formate concentrations are 80-190x10^{-9} M, 200-800x10^{-9} M, and 100-250x10^{-9} M, respectively, from the Sargasso Sea, Biscayne Bay, and Orinoco estuarine water (*Kieber et al*., 1988; *Vaughan and Mopper*, 1990). Should methanol concentrations prove similar to formaldehyde in the surface micro-layer or to formate, they would be on the order of 50x10^{-9} M. This concentration is approximately that required to support the methanol oceanic gross emission rate above.

4. Terrestrial Net Fluxes

Methanol fluxes have been measured above some terrestrial plant canopies including conifer forests (*Schade and Goldstein* 2001;

Baker et al. 2001), tropical rainforest (*Geron et al*., 2001), harvested hayfields (Karl et al. 2001) and an alfalfa field before and after harvesting (*Rinne et al*. 2001, *Warneke et al*., 2002). These investigators measured net methanol fluxes using either the relaxed eddy accumulation technique or eddy covariance methods (e.g. *Wesely and Hicks*, 2000). The reported net methanol fluxes can be used to evaluate the terrestrial methanol source and sink estimates described above. The total terrestrial biogenic source (live vegetation plus plant matter decay) of 300 Tg-methanol yr^{-1} (see Table 4) can be distributed among individual ecosystem types using the model of *Guenther et al.* [1995]. This procedure predicts annual total methanol emissions of 0.44 g m^{-2} for sub-alpine conifer forests, 0.55 g m^{-2} for cool temperate conifer forests, 0.74 g m^{-2} for irrigated croplands, and 3.9 g m^{-2} for tropical rainforests. *Schade and Goldstein* [2001] observed average daily net methanol fluxes of about 15 mg C m^{-2} from July to mid September from a cool temperate conifer forest. The total flux of about 1 g m^{-2} observed for the duration of their study is probably considerably less than the annual total since similar or higher fluxes are expected for at least May and June at this site. The predicted contribution of this landscape to the global annual emission (0.55 g m^{-2}) is lower than the observed net flux. The other studies report fewer observations and are more difficult to extrapolate but the results suggest daily methanol fluxes of about 8 to 13 mg C m^{-2} and annual fluxes of about 0.6 g m^{-2} for sub-alpine conifer forest, 1 g m^{-2} for irrigated crops and 3 g m^{-2} for tropical rainforests. In each case, the net flux estimates based on field measurements are similar to the predictions associated with the global source estimate. Since the observed net flux should be considerably less than the predicted emission at these sites, due to the expected deposition rates, this evaluation demonstrates our limited understanding of the methanol budget for terrestrial landscapes. However, these results argue for a terrestrial ecosystem source that is at the high end of previous estimates.

5. Summary

The mass of methanol in the atmospheric reservoir, the mass rate of methanol sources and sinks, and the estimated atmospheric lifetime of methanol in the free troposphere, MBL, CBL, and in-cloud, are summarized in Table 4. The methanol source and sink total 340 and 270 Tg-methanol yr^{-1}, respectively. The uncertainty in either value remains large, ±200 Tg-methanol yr^{-1}. The sink value derived here is approximately 6 times that estimated by *Singh et al.* [2000] and it is about 3 times their estimated source. This sink value is much closer to a total source calculated using *Guenther et al.*'s biogenic emissions, >280 Tg-methanol yr^{-1}, and this source value was adopted. It is important to note that sources still exceed sinks, here by about 25%, and this will be made larger with the inclusion of an oceanic methanol source. The greatest uncertainties can be found in the estimates of biogenic emissions and dry deposition suggesting continued methanol study is required in this area. Losses of methanol by precipitation and by in-cloud aqueous reaction are noted. These are thought to be small in this analysis but comprise a significant sink when compared with prior total sink estimates. In the case of clouds and seawater, analytical methods are unreported and observations are unavailable with which to begin

to critically assess methanol concentrations in these media and assess their significance in methanol loss. Additional rain and snow methanol measurements are needed to refine precipitation removal estimates.

The implied flux of methanol from the atmosphere to the ocean and its biogeochemical cycling in the surface ocean is intriguing. The amount of methanol introduced from the air exceeds the amount of methane produced in the open ocean column. Add to this methanol, the methanol production argued for in the upper ocean, then these ubiquitous sources could be sustaining methylotrophic organisms throughout the surface ocean.

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Table 1: Estimated biogenic emissions of volatile organic compounds[#], Tg-C yr^{-1}

Species	minimum	maximum	mid-value	percentage
Methane	319	412	366	23
Isoprene	175	503	339	22
Monoterpene family	127	480	304	19
Dimetheylsulfide	15	30	23	1
Ethylene	8	25	17	1
Other reactive VOC's			260	17
Other less reactive VOC's			260	17
Total VOC			1567	100
Biogenic Methanol[&]			100	6
Total Methanol[&]			128	
Total Acetone[@]			59	

[#]*Fall* [1999]

[@]*Jacob et al.* [2002]

[&]this work

Table 2a: Atmospheric Methanol Observations

MEASUREMENT/ESTIMATE	Mean Value	Range	Reference
NEAR-SURFACE, ppt			
Arctic (2/14-3/10; Alert, Nunavut, Canada)	200	41-424	24 hr no sun, *Boudries et al.* [2002]
Arctic (3/10—31; Alert, Nunavut, Canada)	269	42-571	Transition, *Boudries et al.* [2002]
Arctic (4/1-5/1; Alert, Nunavut, Canada)	256	34-594	24 hr sun, *Boudries et al.* [2002]
remote ocean (Pacific and N. Atlantic)	900	200-1200	*Singh et al.* [2000, 2001]
hayfield (Austria)	6000	4000-9000	*Karl et al.* [2001]
urban (Innsbruck Austria)	7500	30-45000	*Holzinger et al.* [2001]
tropical rainforest (Surinam)	1100		*Williams et al* [2001]
urban (San Paulo, Rio de Janeiro, and Salvador, Brazil)		<7600-72000	*de Paula-Pereira et al.* [1999]
aged urban and pine forest day (CA)	10000	4000-10000	*Lamanna and Goldstein* [1999]
boundary layer forest (MA)	20000	5000-37000	*Doskey and Gao* [1999]
rural/forest/field/urban (TN)	11000	3000-22000	*Riemer et al.* [1998]
mountain background (CO)	2000	2000-4000	*Goldan et al.* [1997]
urban/mountain upsloe (CO)	6000	3000-6000	*Goldan et al.* [1997]
rural (Garm.-Part. Germany)	2300	1200-4000	*Leibrock and Slemr* [1997]
urban (Kuwait), 4 sites	55000	43000-65000	*Bouhamra* [1996]
rural (Kuwait), 2 sites	1000	40-1900	*Bouhamra* [1996]
urban (CO)	20000	1000-17000	*Goldan et al.* [1995a]
background estimate (CO)	2000	$1900+0.17*[NO_y]$	*Goldan et al.* [1995a]
fresh urban estimate (CO)	20000	$1900+0.17*[NO_y]$	*Goldan et al.* [1995a]
rural forest day (AL)	11000	1000-20000	*Goldan et al.* [1995b]
rural forest night (AL)	6000	1000-20000	*Goldan et al.* [1995b]
urban (Boston, MA)	17400	7200-47000	*Kelly et al.* [1993]
urban (Houston, TX)	16600	5600-31000	*Kelly et al.* [1993]
industrial area (NC), 3 samples	195000	78500-297000	*Kelly et al.* [1993]
rural (AZ)	2600	+/- 1100	*Snider and Dawson* [1985]
urban (AZ)	7900	+/-2600	*Snider and Dawson* [1985]
Arctic (summer, Pt Barrow, AK)	800	400-1200	*Cavanagh et al.* [1969]
TROPOSPHERE ALOFT, ppt			
Alps (Sonnblick, Austria), 3.1 km	1250	1000-5000	T. Karl (personal communication)
remote ocean, (Pac. and N. Atl.) 2-12 km	600	300-1200	*Singh et al.* [1995, 2000, 2001]
tropical (Surinam)	600		*Williams et al.* [2001]
New England forest (MA), 1-3 km	20000	5000-15000	*Doskey and Gao* [1999]
Rocky Mountains (CO), ~3 km	2000		*Goldan et al.* [1997]
Mauna Loa Observatory (HI), ~3km		500 - 2000	T. Karl (personal communication)
RAIN, nano-Molar			
rural (AZ)	690		*Snider and Dawson* [1985]

Table 2b: Representative Atmospheric Methanol Concentrations, ppt or μM

Boundary Layer, ppt			
Arctic winter/spring	250	30-600	
Arctic summer	800	400-1200	
Background Ocean	900	300-1400	
Background Continent	2000	1000-4000	
Grassland	6000	4000-9000	
Forest	10000	1000-37000	
Urban	20000	30-47000	
Aloft, ppt			
Free Troposphere	600	300-1200	
Rain Estimated Range, micro-Molar (μM)			
Rain Equilibrium Estimates for Temperatures of	0 deg-C	25 deg-C	H; *Snider and Dawson* [1985]
Background Ocean	0.9	0.2	CH_3OH = 900ppt
Urban	20	4	CH_3OH = 20000ppt

Table 3. Measurements of methanol emissions from vegetation

Source	Methanol flux	Methanol flux	Reference
Laboratory	range	mean	
Diverse species (14)	0.2-18.4 µg C g^{-1} h^{-1}	5.4 µg C g^{-1} h^{-1}	*MacDonald and Fall* [1993]
Bean and cottonwood leaves	5-65 µg g^{-1} h^{-1} (bush bean); 5-50 µg g^{-1} h^{-1} (soybean); 1-70 µg g^{-1} h^{-1} (cottonwood)	≈7.5 µg C g^{-1} h^{-1}	*Nemecek-Marshall et al.* [1995]
Aspen leaves (young)	75-114 µg g^{-1} h^{-1}	31 µg C g^{-1} h^{-1}	R. Fall (unpublished)
Mediterranean holm oak (leaf dry wt.); minimum root flooded, maximum young leaf	0.08-1.4 µg C g^{-1} h^{-1}	0.5 µg C g^{-1} h^{-1}	*Holzinger et al.* [2000]
Field			
Grass	0.9-1.3 mg m^{-2} h^{-1}		*Kirstine et al.* [1998]
Clover	9-20 mg m^{-2} h^{-1}		
Grassland		0.46±0.07 mg m^{-2} h^{-1} (noon, 2 yr average; 1.4±0.2 µg g^{-1} h^{-1})	*Fukui and Doskey* [1998]
Sub-alpine conifer forest		≈1 mg m^{-2} h^{-1}	*Baker et al.* [2001]
Pine forest		≈4 mg m^{-2} h^{-1} (daily maximum, 2 mo average)	*Schade and Goldstein* [2001]
Hayfield	1-8.4 mg m^{-2} h^{-1}		*Karl et al.* [2001]
Alfalfa field	Undisturbed: 12.9 mg m^{-2} 24 h^{-1} After cutting (3 different days): 25.5-35.2 mg m^{-2} 24 h^{-1}	≈1 mg m^{-2} h^{-1} (24 h average)	*Warneke et al.* [2002]
Rain forest	1-5 µg C g^{-1} h^{-1} (various leaves)	≈0.5 mg m^{-2} h^{-1}	*Geron et al.* [2002]

Table 4. Estimated Methanol Global Inventory, Tg-methanol, and Its Sources and Sinks, Tg-methanol yr^{-1}

Description	Value	Range	Comment
METHANOL MASS, Tg			
Free Tropsphere	2.5	2.5	600 pptv
Marine BL	0.7	0.5-0.9	Zbl=1km; 900(600-1200) pptv
Continental BL	0.7	0.5-3.5	Zbl=2km; 2000(1500-4000) pptv
Total Mass	3.9	3.5-6.9	
SOURCES, Tg-methanol yr^{-1}			
Primary Anthropogenic	8	5-11	0.17*NOx emissions; after *Goldan et al.* [1995a] and fossil fuel NOx from *Braseur et al.* [1999]
Primary Biogenic	280	50->280	poorly constrained (e.g., >280 Tg-methanol yr^{-1} [*Guenther et al.* [1995, 1999]; 50-125 *Singh et al.* [2000]
Methane Oxidation	30	18-30	18 from *Singh et al.* [2000] and 30 from *Bey et al.* [2001] 3-D models, respectively.
Plant Matter Decay	20	10-40	18-40 *Warneke et al.* [1999]; 10-40 *Singh et al.*, [2000]
Biomass Burning	12	2-32	1.6 (0.6-3.1) % of CO biomass burning emission, *Yokelson et al.*, [1999]; *Goode et al.* [2000]; *Brasseur et al.* [1999]
Ocean	???	0-80	30 Tg-methanol yr-1, assumes oceanic emissions compensate for oceanic dry deposition minus FT-MBL exchange.
Source Total	**345**	**90-490**	
SINKS, Tg-methanol yr^{-1}			
dry deposition land	70	35-210	Vs=estimated from CH3OOH (*Wesley*, 1989), MeOH= 2000 pptv continental background, 10000 pptv grassland/forest; 65 Tg-methanol yr^{-1} spring+summer; 5 Tg-methanol yr^{-1} fall+winter
dry deposition ocean	80	60-150	Vs=0.42 cm/s for wind=5m/s, (1.1 at 10 m/s; est. *Duce et al.*, 1991), MeOH=900 pptv oceanic to 2000 continental background
wet deposition ocean	5	1-16	Equilibrum; H(MeOH) from *Snider and Dawson* [1985], MeOH=900 pptv, precipitation *Peixoto and Oort* [1992]
wet deposition land	5	3-20	Equilibrium; H from *Snider and Dawson* [1985], MeOH=2000 pptv, precipitation *Peixoto and Oort* [1992]
Aqueous HO reaction	10	5-20	lwc=3e-7 L/L; HO=0.2(0.1-0.4)e-12 M; k=1e9; MeOH=900 (2000) pptv; H(MeOH)=1000 M/atm; 50(30)% cloud cover; 0.5(1)km cloud thickness
Gaseous HO reaction	100	25-150	3D model [HO] of *Bey et al.* [2001]: assumed methanol of FT=600 pptv, CBL=2000 pptv, MBL=900 pptv
Sink Total	**270**	**160-570**	
Methanol Lifetimes, days			
gas reaction		18	τ_{OH} based on *Bey et al.* [2001]
cloud reaction		111	τ_{cloud}= 1/(k[HO])/fc/ft/fd; k=1e9 1/M/s; [HO]=0.2e-12 M; fc=HRTL/(1+HRTL); H=1000, RT=22.4, L=3e-7; ft = cloud time fraction 15(10-20)%; fd= fraction of day light 50%;
surface deposition		24	Zbl/Vs/fbl; cont. (Vs=0.4 cm/s; Zbl=2km); ocean (Vs=0.4 cm/s; Zbl=1km); fbl=fraction of time in BL 15(10-20)%
Composite Lifetime		9	gas HO, cloud HO, precipitation, surface deposition

Table 5. Monoalgal Culture Studies of Methanol Producers (after *Milne et al*., 1995)

Organism	Methanol[@]	Isoprene[#]
Diatoms		
Biddulphia mobiliensis	+	+
Phaeodactylum tricornutum	+	+
Thalassiosira weissflogil	+	+
Chaetoceros affinis	+	+
Skeletonema costatum	+	+
Coccolithophores		
Emiliania hyxleyi	+	+
Dinoflagellates		
Amphidinium aperculatum	+	+
Heterocupsa pygmaea	+	+
Others		
Prymnesium parvum	+	+
Synechococcus sp	+	+

+ denotes culture experiment methanol or isoprene was present in culture headspace

[#]*Milne et al*. [1995]; *Riemer* [1998]

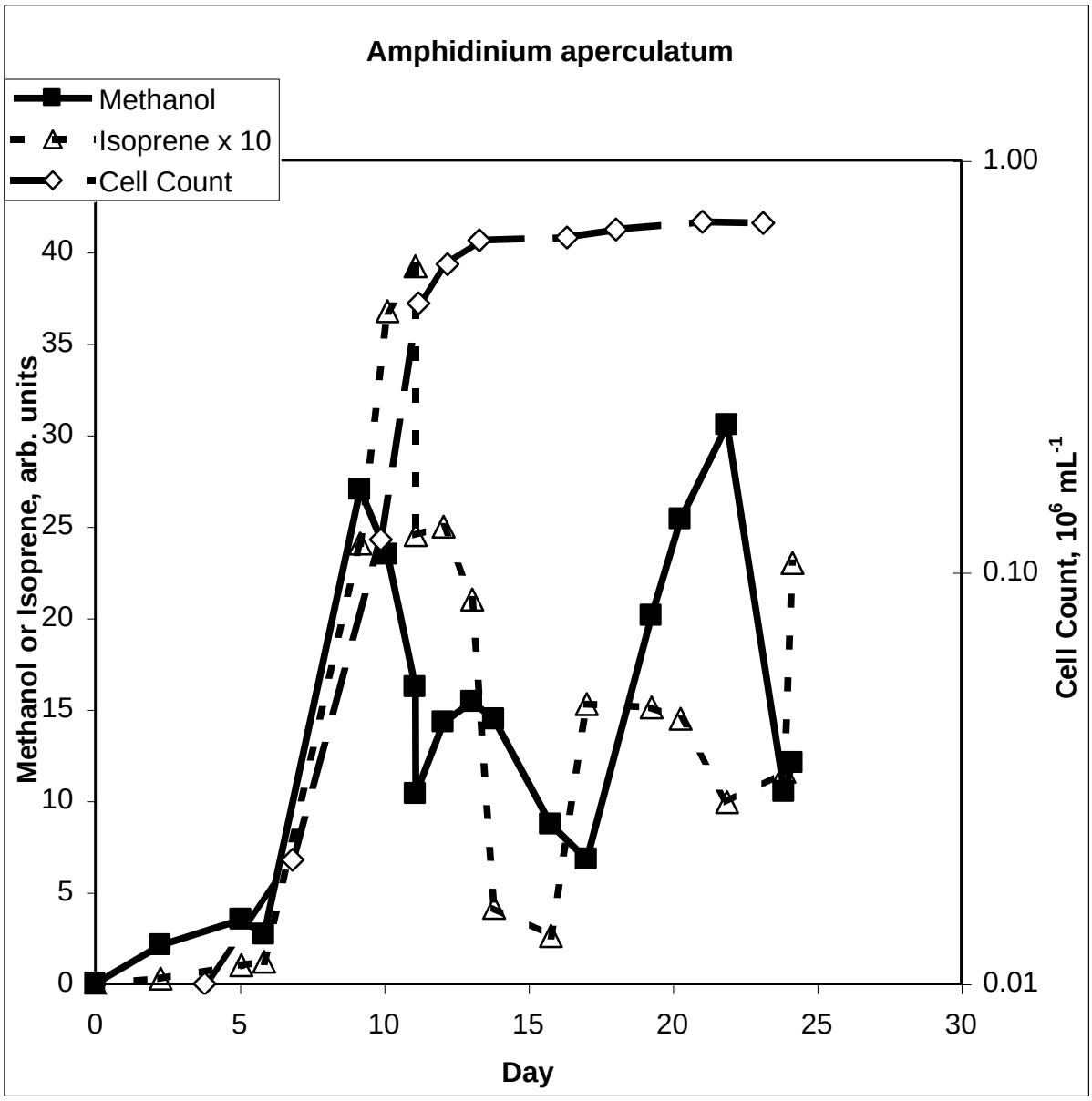

Figure 1. Headspace methanol and isoprene and cell count during laboratory culture experiment with *Amphidinium aperculatum*.