



Global annual methane emission rate derived from its current atmospheric mixing ratio and estimated lifetime

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Abstract. We use the estimated lifetime of methane (CH_4), the current methane concentration, and its annual growth rate to calculate the global methane emission rate. The upper and lower limits of the annual global methane emission rate, depending on loss of CH_4 into the stratosphere and methane consuming bacteria, amounts to 648.0 Mt a^{-1} and 608.0 Mt a^{-1} . These values are in reasonable agreement with satellite and with much more accurate in situ measurements of methane. We estimate a mean tropospheric and mass-weighted temperature related to the reaction rate and employ a mean OH-concentration to calculate a mean methane lifetime. The estimated atmospheric lifetime of methane amounts to 8.28 years and 8.84 years, respectively. In order to improve the analysis a realistic 3D-calculations should be performed.

Keywords. Atmospheric composition and structure (geochemical cycles, middle atmosphere – composition and chemistry, troposphere composition and chemistry)

1 Introduction

Methane (CH_4) is an important greenhouse gas and has a warming potential 25 times per molecule larger than that of carbon dioxide (CO_2). Its atmospheric concentration has more than doubled by anthropogenic impact since the preindustrial time (e.g. Etheridge et al., 1998; Forster et al., 2007; Allan et al., 2007; Kirschke et al., 2013). A large body of publications dealt with the preindustrial methane level (e.g. Rasmussen and Khalil, 1984; Chappellaz et al., 1990; Brook et al., 1996; Etheridge et al., 1998, 2002). The preindustrial level of methane according to Chappellaz et al. (1990), lay

at 0.650 ppmv, Etheridge et al. (1998) derived 0.695 ppmv, and later Etheridge et al. (2002) increased this value to 0.823 ppmv. Kirschke et al. (2013) stated a mixing ratio of 0.830 ppmv close to that value of Etheridge et al. (2002). Natural variations (increasing for wet and warm periods) also influenced the methane level in the past, so that no constant concentration occurred in the preindustrial time (Rasmussen and Khalil, 1984), but the mixing ratio varied around a mean value. The increase of the methane concentration did stagnate, or it increased very slowly, since the nineties of the past century (e.g. Dlugokencky et al., 2003; Simpson et al., 2006). It increases slightly in present time (e.g. Khalil et al., 2007; Frankenberg et al., 2011). Bergamaschi et al. (2013) found a significant rise of methane and its emission again since 2006 which is, however, essentially smaller than the strong increase in the 20th century. The greatest part of the recent increase is contributed to the tropics and mid-latitude of the Northern Hemisphere (Bergamaschi et al., 2013).

The current tropospheric mixing ratio lies between 1.75 and 1.8 ppmv (Krol et al., 1998; Dlugokencky et al., 2003; Frankenberg et al., 2005; Khalil et al., 2007; Frankenberg et al., 2011; Kirschke et al., 2013), after Climate Change 2007: Working Group I: The Physical Science Basis, IPCC Fourth Assessment Report: Climate Change 2007 in 2005 1774.62 ± 1.22 ppbv. A surface-based monitoring by four networks exhibits very consistent observations. In these networks are involved NOAA (National Oceanic and Atmospheric Administration, Dlugokencky et al., 2011), AGAGE (Advanced Global Atmospheric Gases Experiment, Rigby et al., 2008), CSIRO (Commonwealth Scientific and Industrial Organization, Francey et al., 1999), and UCR (University of California Irvin, Simpson et al., 2012). According to their

accurate observations the mixing ratio in 2010 amounted to 1799 ± 2 ppbv.

There are numerous natural and anthropogenic sources of methane. In the past, various groups try to estimate the contribution of different individual sources. If the lifetime of methane and its concentration in the atmosphere are known then one can calculate the global emission rate.

The lifetime of methane was estimated to range between 8 and 12 years: 10 ± 2 years according to Krol et al. (1998); 7.9 years increasing to 8.4 years in 2050 according to Lelieveld et al. (1998); 8.7 ± 1.3 years according to the fourth IPCC assessment report (2007); and 9.2 years in the 5th Assessment Report (2011). Prinn et al. (2005) published $9.3 (+0.7, -0.6)$ years and Prather et al. (2012) estimated 9.1 ± 0.9 years. John et al. (2012) list a survey of estimations about the change in methane lifetime since the preindustrial time. The lifetime can be estimated if the mean hydroxyl (OH) concentration, the tropospheric temperature, and some additional methane sinks are known. The main of additional (secondary) sinks are losses by methane consuming bacteria (5 %) and loss into the stratosphere (7 %) (Reay et al., 2007). Lawrence et al. (2001) used smaller values (1 %) for the loss into the stratosphere. A possible methane sink due to oxidation by atomic chlorine in the marine boundary layer was introduced by Allan et al. (2001, 2007), but its real share in the methane destruction is still under discussion. Other minor sinks are the reactions with other constituents such as O(¹D), etc.

Prather et al. (2012) estimated for $\tau_{\text{CH}_4\text{-OH}} = 11.2 \pm 1.3$ years, for $\tau_{\text{CH}_4\text{-bacteria}} = 120$ years, for $\tau_{\text{CH}_4\text{-strat}} = 150$ years, and for a possible oxidation by atomic chlorine in the marine atmospheric boundary layer 200 years (according to Allan et al., 2007). For the period 1979–1993 Dentener et al. (2003) calculated for $\tau_{\text{CH}_4\text{-OH}} = 9.0 \pm 1.3$ years. For the period 1978–2004 Prinn et al. (2005) estimated a lifetime of $10.2 (+0.9, -0.7)$ years. A similar value of 10.2 ± 1.7 years found Fiore et al. (2009). Other estimations range in the same order: 9.8 ± 1.6 years (Vougarakis et al., 2013), $9.9 (+1.66, -1.76)$ years (Stevenson et al., 2006).

The main loss of CH₄ in the troposphere is the reaction with OH. OH reacts with CH₃CCl₃ (methyl chloroform MCF). The reaction of OH with methyl chloroform as an efficient radical sink modulating the long-term tropospheric OH concentration was widely discussed in the literature (e.g. Prinn et al., 1995, 2001; Houweling et al., 1999; Dentener et al., 2003; Krol et al., 2003; Bousquet et al., 2005, 2006; John et al., 2012). In this paper we do not calculate the balance of OH but use published estimations of OH.

2 Calculations and results

The methane lifetime can be estimated via the reaction with OH by using a globally averaged OH concentration and considering additional sinks (e.g. Prinn et al.,

2005; Prather et al., 2012; John et al., 2012). The reaction rate of OH with methane amounts to $r_1 = 2.45 \times 10^{-12} \exp(-1775/T) \text{ cm}^{-3} \text{ s}^{-1}$ (Sanders et al., 2006), and rises with increasing temperature. The expression

$$\tau_{\text{CH}_4} = 1 / (r_1 \cdot [\text{OH}]_{\text{mean}} + S) \quad (1)$$

is the inverse reduced loss term of methane and stands for its lifetime or also called residence-time, where S represents additional sinks. We employ for S values only sinks by bacteria and loss into the stratosphere, published by Reay et al. (2007) and Lawrence et al. (2001) as upper (5 % + 7 %) and lower (5 % + 1 %) limit cases, respectively. Note, we take into account only globally averaged values and neglect minor reactions such as a possible reaction with chlorine (Prather et al., 2012). Although the lifetime amounts to approximately a decade, the mixing processes are not fast enough to distribute methane evenly over the whole troposphere. We use a mean temperature (T_{mean}) related to the temperature acting in the reaction rate. The mass-weighted temperature, with respect to the reaction rate, is somewhat larger than the mass-weighted tropospheric mean temperature (T_{trop}). Taking into account additional sources S in a coefficient β , the mean lifetime is then

$$\tau_{\text{CH}_4} = 1 / (\beta \cdot r_1(T_{\text{mean}}) \cdot [\text{OH}]_{\text{mean}}) \quad (2)$$

in case where $[\text{OH}]_{\text{mean}}$ is known. The factor β amounts to 1.136 and 1.0638 for the additional sinks of 12 % (5 % + 7 %) and 6 % (5 % + 1 %), respectively. T_{mean} is essentially smaller than the global mean surface temperature because T decreases with increasing height.

The mean concentration of OH derived from several groups listed in Table 1 by Lawrence et al. (2001) is about $[\text{OH}]_{\text{mean}} = 10^6 \text{ cm}^{-3}$. We use a value of $1.16 \times 10^6 \text{ cm}^{-3}$, according to Spivakovsky et al. (2000). For instance, an OH-concentration close to $1 \times 10^6 \text{ cm}^{-3}$ ($0.973 \times 10^6 \text{ cm}^{-3}$) follows with a mean reaction related temperature from $\tau_{\text{CH}_4\text{-OH}} = 11.2$ years (Prather et al., 2012). In the tropics, the OH-concentration is essentially larger than outside of it (Lawrence et al., 2001; Labrador et al., 2004; Kirschke et al., 2013). The non-uniform latitudinal distribution of OH is one problem in all budget calculations. Equation (2) has a remarkable temperature sensitivity which lies in the order of 2–3 % per 1 K (2.5 % per K for $T = 263.5 \text{ K}$, the mean reaction related temperature of the troposphere) and increases with decreasing temperature. The mean mass-weighted tropospheric temperature can be calculated by using the expression

$$T_{\text{trop}} = \int_0^{12 \text{ km}} T(z) m(z) dz / \int_0^{12 \text{ km}} m(z) dz \quad (3)$$

integrated in the borders of 0 to 12 km, averaged over the whole troposphere. Here $m(z)$ is the mean mass of air per

cubic centimeter at the height z . The mean height of the troposphere ranges coarsely in the order of 12 km. 50 % of the atmospheric mass lies below 5.5 km, approximately. The mean surface temperature amounts to $T_{\text{surf}} = 287.76$ K, and the mean lapse rate is $\gamma_{\text{mean}} = 6.5$ K km⁻¹. About $\Delta T = 33$ K in the atmosphere corresponds to 1 km scale height.

$$T_{\text{trop}} = \frac{\int (T_{\text{surf}} - \gamma_{\text{mean}} \cdot z) \exp\left(-\frac{z \cdot \Delta T}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) dz}{\int \exp\left(-\frac{z \cdot \Delta T}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) dz} \quad (4)$$

$$\exp\left(-\frac{1775}{T_{\text{mean}}}\right) = \frac{\int \exp\left(\frac{-1775}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) \exp\left(-\frac{z \cdot \Delta T}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) dz}{\int \exp\left(-\frac{z \cdot \Delta T}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) dz} \quad (5)$$

It follows that

$$T_{\text{mean}} = -\frac{1775}{\ln\left(\frac{\int \exp\left(-\frac{1775}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) \exp\left(-\frac{z \cdot \Delta T}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) dz}{\int \exp\left(-\frac{z \cdot \Delta T}{T_{\text{surf}} - \gamma_{\text{mean}} \cdot z}\right) dz}\right)} \quad (6)$$

Using these coarse values, the mean mass-weighted temperature of the troposphere amounts to $T_{\text{trop}} = -13.32$ °C = 259.83 K, and the mean reaction rate related temperature is $T_{\text{mean}} = -9.65$ °C = 263.5 K, and correspond to the heights $z(T_{\text{trop}}) = 4.3$ km and $z(T_{\text{mean}}) = 3.58$ km, respectively.

We employ the lifetime of methane, the current methane concentration and its growth rate to derive the global methane emission rate E_{CH_4} . The balance equation for methane (analogously for other minor constituents) resolved to the emission rate can be written as (e.g. Kirschke et al., 2013; Sonnemann and Grygalashvily, 2013):

$$E_{\text{CH}_4} = \frac{d[\text{CH}_4]}{dt} + \frac{[\text{CH}_4]}{\tau_{\text{CH}_4}} \quad (7)$$

In case of equilibrium ($d[\text{CH}_4]/dt = 0$) the annual emission rate is

$$E_{\text{CH}_4} = \alpha[\text{CH}_4]_{\text{mix}} H_{\text{eff}} S_{\text{Earth}} / \tau_{\text{CH}_4}, \quad (8)$$

where E_{CH_4} stands for the global emission rate of methane, $[\text{CH}_4]_{\text{mix}}$ represents the globally averaged tropospheric mixing ratio of methane at about 1.8 ppmv, H_{eff} means the effective (or mean) density scale height of about 8 km (1.033 kg air in a beam of 1 cm² at surface area), and S_{Earth} considers the Earth's surface area of 5.1×10^{18} cm², and finally α is a factor which converts the mixing ratio given in ppmv into mass in Mt a⁻¹. Using the mol volume and the molar

mass of methane of 16.04 g mol⁻¹ the factor $\alpha = 16.04 \times 10^{-6}/22\,414$.

Figure 1 shows the global methane emission rate for a current atmospheric methane concentration of 1.8 ppmv, depending on lifetime including an annual growth rate of methane of 5 ppbv a⁻¹ and corresponding to an increasing emission of 1.457 Mt a⁻¹. (A methane increase due to a growth rate of 5 ppbv a⁻¹ corresponds to an increase of the warming potential of $0.005 \times 25 = 0.125$ ppmv CO₂, coarsely 5 % of the increase due to the annual CO₂ growth rate.)

From these values, there follows an annual methane emission rate of $E_{\text{CH}_4} = 446.66$ Mt a⁻¹ for a lifetime of 12 years, or 538.39 Mt a⁻¹ for $\tau_{\text{CH}_4} = 10$ years and for $\tau_{\text{CH}_4} = 8$ years 672.99 Mt a⁻¹. Presently there is no equilibrium ($d[\text{CH}_4]/dt > 0$), thus, a correction must be considered. For an annual increase of 10 ppbv, according to Eq. (7), the correction amounts to $0.01 \times 524.568/1.8 = 2.914$ Mt a⁻¹, ergo the annual emission amounts to 541.3 Mt a⁻¹ for the 10 year lifetime case.

With the mean tropospheric OH concentration of Spivakovsky et al. (2000) we get an annual global methane emission rate of 648.0 Mt a⁻¹ for the first estimation of methane loss (7 %) into the stratosphere and 608.0 Mt a⁻¹ for the second (1 %) case. The last value agrees fairly well with model calculations by Lelieveld et al. (1998) who estimated about 600 Mt a⁻¹. These values are in reasonable (≈ 10 %) agreement with satellite measurements of methane. The estimated atmospheric lifetime of methane then amounts to 8.28 years and 8.84 years, respectively.

3 Discussion

The growth rate varied at around 14 ppbv a⁻¹ before 1990 (Blake and Rowland, 1988; Dlugokencky et al., 1998; Simpson et al., 2002), and it amounts presently to few ppbv a⁻¹ (van Weele, 2010; Bergamaschi et al., 2013). After a period of decreasing growth rate (partly even negative), the growth rate increased again in 2007 to 8.3 ± 0.6 ppbv a⁻¹ (Dlugokencky et al., 2009). But 2007 was an exceptional year, marked among other peculiarities by a strong decrease of the Arctic ice covering and a very warm year over the Siberian wetland. In 2008, the global average increase of methane amounted to 4.4 ± 0.6 ppbv a⁻¹ (Dlugokencky et al., 2009) and remained coarsely on this level after this time (Bergamaschi et al., 2013). According to Kirschke et al. (2013) the growth rate amounted to 11.3–12.3 ppbv a⁻¹ in the 1980s, 4.9–6.5 ppbv a⁻¹ in the 1990s, and 2.3–3.6 ppbv a⁻¹ in the 2000s indicating the slow down of the growth rate. The increase came mainly from the tropical wetland. Obviously, the varying methane growth rates are also connected with global climatic variations. Events such as El Niño, La Niña, or the eruptions of volcano like Mt. Pinatubo and others considerably influence the growth rate. Therefore

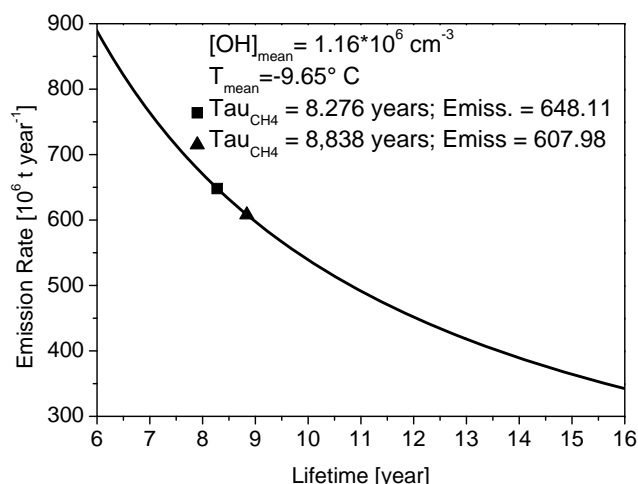


Fig. 1. Global methane emission rate versus lifetime of methane for a current atmospheric methane concentration of 1.8 ppmv. This includes an annual growth rate of methane of 5 ppbv a^{-1} corresponding to an increasing emission of 1.457 Mt a^{-1} . The lifetime depends inversely on the mean OH concentration and the tropospheric temperature.

it is not meaningful for the assessment of the methane trend to consider the growth rate of isolated years.

OH is called the atmosphere cleaner, as it quickly reacts with a large number of environmental pollutants. It determines the atmospheric oxidizing efficiency. OH is produced by the reaction $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$, and $\text{O}(^1\text{D})$ results from the photolysis of ozone (O_3). Both methane and ozone are greenhouse gases. An increase of tropospheric ozone reduces the methane concentration. Among other reactions, such as OH with CH_3CCl_3 , a sink of OH is the reaction with CO. The last reaction is included in the smog formation cycle of ozone but in the smog formation cycle itself no hydrogen radical loss takes place. The reactions $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ and $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ are followed by the reaction $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$, which forms back OH, so that the balance of OH is more intricate as inferred from the pure OH loss reaction with CO only. A real loss results from the reaction $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ forming highly soluble nitric acid (HNO_3). In the past, the lifetime of methane probably shortened due to an increase of tropospheric ozone and consequently of OH as well as a slight temperature growth. A small increase in the methane growth rate can be compensated by an adequate decrease of its lifetime.

If using the preindustrial value as the natural level (caused by wetland, termites, methane hydrates, phytoplankton in the ocean (e.g. Sieburth and Donaghay, 1993; Zindler et al., 2013), permafrost soil, and wild animals), the difference should have anthropogenic sources such as livestock, rice cultivation, coal mining, oil and gas, landfills, biomass burning, waste water, and others. However, natural sources have also been influenced by anthropogenic activities like the

reduction of the area of natural wetlands or the impact on the permafrost soil. According to Stern and Kaufmann (1996), a considerable decrease of the natural emission occurred between 1860 and 1990. The decline amounts to roughly a third of its preindustrial value. Van Weele (2010) published values for anthropogenic and natural sources derived from SCIAMACHY onboard the ENVISAT satellite of 395 and 198 Mt a^{-1} (total 593 Mt a^{-1}), respectively. Lelieveld et al. (1998) estimated about 600 Mt a^{-1} , with an anthropogenic share of 70%. Etheridge et al. (1998) derived a value of the global emission rate of 560 Mt a^{-1} , which tended to stabilize at this level. The budget calculations for the years after 2000 result in a minimum-maximum range of 526–569 (mean 548) Mt a^{-1} (Kirschke et al., 2013). If summing up all bottom-up emissions they get a value of 678 Mt a^{-1} 20% larger which possibly overestimates individual sources.

Lelieveld et al. (1998) estimated a relatively small lifetime of 7.9 years. A survey of estimated lifetimes of methane due to reactions with OH can be found in the paper by John et al. (2012). The values range between 9 to 11.2 years. The consideration of other methane sinks yields according to Prather et al. (2012) a lifetime of 9.1 ± 0.9 years. The emission rate would agree with satellite measurements for a somewhat smaller mean tropospheric OH-concentration, a cooler mean temperature, or a larger loss by bacteria, by reaction with chlorine and transport into the stratosphere, respectively. However, due to the unequal latitudinal and vertical distribution of methane, hydroxyl and chlorine as well as the transport into the stratosphere a more realistic 3D-calculation could also change the computed emission rate and the lifetimes in certain borders.

The value of the anthropogenic methane emission also agrees fairly well with that value inferred by Stern and Kaufmann (1996), taking into consideration that methane has increased slightly since that time. The SCIAMACHY-value would agree with our calculations for a lifetime of methane of 9.1 years (close to Prather et al., 2012) and, consequently, with somewhat smaller mean OH-concentrations of $[\text{OH}]_{\text{mean}} = 1.055 \times 10^6 \text{ cm}^{-3}$ or alternatively enhanced secondary methane sinks. Denman et al. (2007) published total emission rates of $582 \pm 87 \text{ Mt a}^{-1}$ with 60% anthropogenic share. This value also points to a somewhat larger lifetime.

A small decline of the methane lifetime should result, as previously mentioned, from the increase of tropospheric ozone. An increase of the atmospheric humidity points in the direction of increased OH formation. A possible increase certainly has different causes than CO, NO_x , H_2 , and MCF, and many other sinks for OH have also changed in the past. In particular, the increasing CH_4 concentration is a sink of OH resulting in a cumulative feedback (John et al., 2012). Krol et al. (1998) derived a positive OH trend of most likely $0.46\% \text{ a}^{-1}$. Also John et al. (2012) reported about a small increase of OH of $3\% \text{ a}^{-1}$. The lifetime of methane decreased due to OH destruction, according to Krol et al. (1998), from

9.2 to 8.6 years from 1978 to 1993. Lelieveld et al. (1998) reported that the lifetime of methane increased by 25–30% during the past 150 years to the current value of 7.9 years, and will further increase by about 6% until 2050, then reaching 8.4 years. Note that both the production and the sinks have changed in the past, so it is not justified to extrapolate a trend found for a limited interval.

4 Conclusions

A precise knowledge of the lifetime and the mixing ratio of methane are the preconditions to calculate its annual emission rate. The published range of uncertainty amounts to $\pm 20\%$. If the emission rate is known, one can split the sum into the partial emission rates of the individual natural and anthropogenic sources. The reason for a slowdown (or stop) of the methane increase can result from a reduced growth rate of methane and/or from a reduction of the methane lifetime due to an increase of [OH] and/or warming of the atmosphere, compensating the growth rate of emission and/or other impacts on the loss term.

The estimations are, of course, relatively coarse. A 3D-calculation taking into account the real global distribution of the temperature and the estimated OH-concentration depending on latitude, height and local time could improve the accuracy of this estimation. Due to the high temperature sensitivity of the OH-CH₄-reaction rate the consideration of the real temperature decreasing with altitude is rather important. A global methane emission rate of 648.0 Mt a⁻¹ and 608.0 Mt a⁻¹ (7% and 1% methane loss into the stratosphere, respectively) and a mean methane lifetime of ~ 8.28 and 8.84 years result from our analysis of the present atmospheric concentrations of methane, mean tropospheric OH, and the percentage share of the secondary methane sinks.

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References

Allan, W., Lowe, D. C., and Caine, J. M.: Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of $\delta^{13}\text{C}$ in methane, *Geophys. Res. Lett.*, 28, 3239–3242, 2001.

Allan, W., Struthers, H., and Lowe, D. C.: Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with Southern Hemisphere measurements, *J. Geophys. Res.*, 112, D04306, doi:10.1029/2006JD007369, 2007.

Bergamaschi, P., Houweling, S., Segers, A., Krol, M., Frankenberg, C., Scheepmaker, R. A., Dlugokencky, E., Wofsy, S. C., Kort, E. A., Sweeney, C., Schuk, T., Brenninkmeyer, Chen, H., Beck, V., and Gerbig, C.: Atmospheric CH₄ in the first decade of

the 21st century: Inverse modeling analysis using SCIAMACHY satellite retrievals and NOAA surface measurements, *J. Geophys. Res.*, 118, 7350–7369, doi:10.1002/jgrd.50480, 2013.

Blake, D. R. and Rowland F. S.: Continuing world-wide increase in tropospheric methane, 1978–1987, *Science*, 239, 1129–1131, 1988.

Bousquet, P., Hauglustaine, D. A., Peylin, P., Carouge, C., and Ciais, P.: Two decades of OH variability as inferred by an inversion of atmospheric transport and chemistry of methyl chloroform, *Atmos. Chem. Phys.*, 5, 2635–2656, doi:10.5194/acp-5-2635-2005, 2005.

Bousquet, P., Ciais, P., Miller, J. B., Dlugokencky, E. J., Hauglustaine, D. A., Prigent, C., Van der Werf, G. R., Peylin, P., Brunke, E. G., Carouge, C., Langenfelds, R. L., Lathiere, J., Papa, F., Ramonet, M., Schmidt, M., Steele, L. P., Tyler, S. C., and White, J.: Contribution of anthropogenic and natural sources to atmospheric methane variability, *Nature*, 443, 439–443, 2006.

Brook, E. J., Sowers, T., and Orchado, J.: Rapid variations in atmospheric methane concentration during past 110,000 years, *Science*, 273, 1087–1091, 1996.

Chappellaz, J., Barnola, J. M., Raynaud, D., Korotkevich, Y. S., and Lorius, C.: Ice-Core Record of Atmospheric Methane over the Past 160,000 Years, *Nature*, 345, 127–131, doi:10.1038/345127a0, 1990.

Denman, K. L., Brasseur G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickenson, R. E., Heinze, C., Holland, E., Jacob, D. J., Lohmann, U., Ramachandran, S., da Silva Dias, P. L., Wofsy, S. C., and Zhang, X.: Couplings between changes in the climate system and biochemistry, in: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge UK and New York, NY, USA, 499–587, 2007.

Dentener, F., Peters, W., Krol, M., van Weele, Bergamaschi, P., and Lelieveld, J.: Inter-annual variability and trend of CH₄ lifetime as a measure for OH change in the 1979–1993 time period, *J. Geophys. Res.*, 108, 4442, doi:10.1029/2002JD002916, 2003.

Dlugokencky, E. J., Masarie, K. A., Lang, P. M., and Tans, P. P.: Continuing decline in the growth rate of the atmospheric methane burden, *Nature*, 393, 447–450, doi:10.1038/30934, 1998.

Dlugokencky, E. J., Houweling, S., Bruhwiler, L., Masarie, K. A., Lang, P. M., Miller, J. B., and Tans, P. P.: Atmospheric methane levels off: Temporary pause or a new steady-state?, *Geophys. Res. Lett.*, 30, 1992, doi:10.1029/2003GL018126, 2003.

Dlugokencky, E. J., Bruhwiler, L., White, J. W. C., Emmons, L. K., Novelli, P. C., Montzka, S. A., Masarie, K. A., Lang, P. M., Crotwell, A. M., Miller, J. B., and Gatti, L. V.: Observational constraints on recent increases in the atmospheric CH₄ burden, *Geophys. Res. Lett.*, 36, L18803, doi:10.1029/2009GL039780, 2009.

Dlugokencky, E. J., Nisbet, E. G., Fisher, R., and Lowry, D.: Global atmospheric methane: budget change and dangers, *Philos. T. Roy. Soc. A*, 369, 2058–2072, 2011.

Etheridge, D. M., Steele, L. P., Francey, R. J., and Langenfelds, R. L.: Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions climatic variability, *J. Geophys. Res.*, 103, 15979–15993, 1998.

- Etheridge, D. M., Pearman, G. I., and Fraser, P. J.: Change in the tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core, Wiley Online Library, doi:10.1034/j.1600-0889.1992.t01-3-00006.x, 2002.
- Fiore, A. M., Dentener, F. J., Wild, O., Covelier, C., Schultz, M. G., Hess, P., Textor, C., Schulz, M., Doherty, R. M., Horowitz, L. W., MacKenzie, I. A., Sanderson, M. G., Shindell, D. T., Stevenson, D. S., Szopa, S., Van Dingenen, R., Zeng, G., Ather-ton, C., Bergmann, D., Bey, I., Carmichael, G., Collins, W. J., Duncan, B. N., Faluvegi, G., Folberth, G., Gauss, M., Gong, S., Hauglustaine, D., Holloway, T., Isaksen, I. S. A., Jacob, D. J., Jonson, J. E., Kaminski, J. W., Keating, T. J., Lupu, A., Marmer, E., Montanaro, V., Park, R. J., Pitari, G., Pringle, K. J., Pyle, J. A., Schroeder, S., Vivanco, M. G., Wind, P., Wojcik, G., Wu, S., and Zuber, A.: Multimodel estimates of intercontinental source-receptor relationships for ozone pollution, *J. Geophys. Res.*, 114, D04301, doi:10.1029/2008JD010816, 2009.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: Changes in atmospheric constituents and in radiative forcing, in: *Climate Change 2007*, edited by: Solomon, S., Qin, D., Man-ning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 129–234, 2007.
- Francey, R. J., Steele, L. P., Langenfelds, R. L., and Pak, B. C.: High-precision long-term monitoring of relatively active and related trace gases at surface sites and from aircraft in the southern hemisphere atmosphere, *J. Atmos. Sci.*, 56, 278–285, 1999.
- Frankenberg, C., Meirink, J. F., van Weele, M., Rasmussen, R. K., Platt, U., and Wagner, T.: Assessing methane emission from global spaceborne observations, *Science*, 308, 1010–1014, doi:10.1126/science.1106644, 2005.
- Frankenberg, C., Aben, I., Bergamaschi, P., Dlugokencky, E. J., van Hees, R., Houweling, S., van der Meer, P., Snel, R., and Tol, P.: Global column-averaged methane mixing ratios from 2003 to 2009 as derived from SCIAMACHY: Trends and variability, *J. Geophys. Res.*, 116, D04302, doi:10.1029/2010JD014849, 2011.
- Houweling, S., Kaminsky, T., Dentener, F., Lelieveld, J., and Heinmann, M.: Inverse modelling of methane sources and sinks using adjoint of a global transport model, *J. Atmos. Res.*, 104, 26137–26160, 1999.
- IPCC Fourth Assessment Report: Climate Change, 2007.
- IPCC Fifth Assessment Report: Renewable Energy Sources and Climate Change Mitigation (AR5), 2011.
- John, J. G., Fiore, A. M., Naik, V., Horowitz, L. W., and Dunne, J. P.: Climate versus emission drivers of methane lifetime against loss by tropospheric OH from 1860–2100, *Atmos. Chem. Phys.*, 12, 12021–12036, doi:10.5194/acp-12-12021-2012, 2012.
- Khalil, M. A. K., Butenhoff, C. L., and Rasmussen, R. A.: Atmospheric Methane: Trends and Cycles of Sources and Sinks, *Environ. Sci. Technol.*, 41, 2131–2137, 2007.
- Kirschke, S., Bousquet, P., Ciais, P., Marielle Saunoy, M., Canadell, J. G., Dlugokencky, E. J., Bergamaschi, P., Bergmann, D., Blake, D. R., Bruhwiler, L., Cameron-Smith, P., Castaldi, S., Chevalier, F., Feng, L., Fraser, A., Fraser, P. J., Heimann, M., Hodson, E. L., Houweling, S., Josse, B., Krümmel, P. B., Lamarque, J.-F., Langenfelds, R. L., Le Quééré, C., Naik, V., O'Doherty, S., Palmer, P. I., Pison, I., Plummer, D., Poulter, B., Prinn, R. G., Rigby, M., Ringeval, B., Santini, M., Schmidt, M., Shindell, D. T., Simpson, I. J., Spahni, R., Steele, L. P., Strode, S. A., Sudo, K., Szopa, S., van der Werf, G. R., Voulgarakis, A., van Weele, M., Weiss, R. F., Williams, J. E., and Zeng, G.: Three decades of global methane sources and sinks, *Nat. Geosci.*, 8, 813–823, doi:10.1038/NNGEO1955, 2013.
- Krol, M. and Lelieveld, J.: Can the variability of tropospheric OH be deduced from measurements of 1,1,1-trichloroethane (methyl chloroform)?, *J. Geophys. Res.*, 108, 4125, doi:10.1029/2002JD002423, 2003.
- Krol, M., van Leeuwen, P. J., and Lelieveld, J.: Global OH trend inferred from methylchloroform measurements, *J. Geophys. Res.*, 103, 10697–10711, doi:10.1029/98JD00459, 1998.
- Labrador, L. J., von Kuhlmann, R., and Lawrence, M. G.: Strong sensitivity of the global mean OH concentration and the tropospheric oxidizing efficiency to the source of NO_x from lightning, *Geophys. Res. Lett.*, 31, L06102, doi:10.1029/2003GL019229, 2004.
- Lawrence, M. G., Jöckel, P., and von Kuhlmann, R.: What does the global mean OH concentration tell us?, *Atmos. Chem. Phys.*, 1, 37–49, doi:10.5194/acp-1-37-2001, 2001.
- Lelieveld, J., Crutzen, P. G., and Dentener, F. G.: Changing concentration, lifetime and climate forcing of atmospheric methane, *Tellus B*, 50, 128–150, doi:10.1034/j.1600-0889.1998.t01-1-00002.x, 1998.
- Prather, M. J., Holmes, C. D., and Hsu, J.: Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry, *Geophys. Res. Lett.*, 39, L09803, doi:10.1029/2012GL051440, 2012.
- Prinn, R. G., Weiss, R. F., Miller, B. R., Huang, J., Alyea, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E., and Simmonds, P. G.: Atmospheric trends and lifetime of CH₃CCl₃ and global OH concentrations, *Science*, 269, 187–192, 1995.
- 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.: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science*, 293, 1882–1888, doi:10.1126/science.1058673, 2001.
- Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Reimann, S., Salameh, P., O'Doherty, S., Wang, R. H. J., Porter, L. W., Miller, B. R., and Krümmel, P. B.: Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, *Geophys. Res. Lett.*, 32, L07809, doi:10.1029/2004GL022228, 2005.
- Rasmussen, R. A. and Khalil, M. A. K.: Atmospheric methane in recent and ancient atmospheres: concentrations, trends, and inter-hemispheric gradient, *J. Geophys. Res.*, 89, 11599–11605, 1984.
- Reay, D., Hewitt, C. N., Smith, K., and Grace, J.: *Greenhouse Gas Sinks*, CABI, Oxfordshire, 2007.
- Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfelds, R. L., Huang, J., Cunnold, D. M., Steele, L. P., Krümmel, P. B., Weiss, R. F., O'Doherty, S., Salameh, P. K., Wang, H. J., Harth, C. M., Mühle, J., and Porter, L. W.: Renewed growth of atmospheric methane, *Geophys. Res. Lett.*, 35, L22805, doi:10.1029/2008GL036037, 2008.
- Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Huie, R. E., Orkin, V. L., Moortgat, G. K., Wine, P. H., Ravishankara, A. R., Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: Chemical kinetics and photochemical data for use in stratospheric mod-

- eling, JPL Publication 06-2, Evaluation Number 15, California Institute of Technology, Pasadena, California, USA, 2006.
- Sieburth, J. McN. and Donaghay, P. L.: Planctonic methane production and oxidation within in the algal maximum of the pycnocline: seasonal fine-scale observations in an anoxic estuarine basin, *Marine Ecology Progress Series*, 100, 3–15, 1993.
- Simpson, I. J., Blake, D. R., Rowland, F. S., and Chen, T.-Y.: Implications of the recent fluctuations in the growth rate of tropospheric methane, *Geophys. Res. Lett.*, 29, 117.1–117.4, doi:10.1029/2001GL014521, 2002.
- Simpson, I. J., Rowland, F. S., Meinardi, S., and Blake, D. R.: Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane, *Geophys. Res. Lett.*, 33, L22808, doi:10.1029/2006GL027330, 2006.
- Simpson, I. J., Andersen, M. P. S., Meinardi, S., Bruhwiler, L., Blake, N. J., Helmig, D., Rowland, F. S., and Blake, D. R.: Long-term decline of global atmospheric ethane concentrations and implications for methane, *Nature*, 488, 490–494, 2012.
- Sonnemann, G. R. and Grygalashvily, M.: Effective CO₂ lifetime and future CO₂ levels based on fit function, *Ann. Geophys.*, 31, 1591–1596, doi:10.5194/angeo-31-1591-2013, 2013.
- 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.: Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, 105, 8931–8980, 2000.
- Stern, D. I. and Kaufmann, R. K.: Estimates of global anthropogenic methane emissions 1860–1993, *Chemosphere*, 33, 159–176, 1996.
- Stevenson, D. S., Dentener, F. G., Schultz, M. G., Ellingsen, K., van Noije, T. P. C., Wild, O., Zeng, G., Amann, M., Atherton, C. S., Bell, N., Bergmann, D. J., Bey, I., Butler, T., Cofala, J., Collins, W. J., Derwent, R. G., Doherty, R. M., Drevet, J., Eskes, H. J., Fiore, A. M., Gauss, M., Hauglustaine, D. A., Horowitz, L. W., Isaksen, I. S. A., Krol, M. C., Lamarque, J.-F., Lawrence, M. G., Montanaro, V., Müller, J.-F., Pitari, G., Prather, M. J., Pyle, J. A., Rast, S., Rodriguez, J. M., Sanderson, M. G., Savage, N. H., Shindell, D. T., Strahan, S. E., Sudo, K., and Szopa, S.: Multimodel ensemble simulations of present-day and near future tropospheric ozone, *J. Geophys. Res. Atmos.*, 111, D08301, doi:10.1029/2005JD006338, 2006.
- van Weele M.: Assessing methane emissions from global spaceborne observations, report: Koninklijk Nederlands Meteorologisch Instituut Ministerie van Infrastructuur en Milieu, 2010.
- Voulgarakis, A., Naik, V., Lamarque, J.-F., Shindell, D. T., Young, P. J., Prather, M. J., Wild, O., Field, R. D., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsøren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Folberth, G. A., Horowitz, L. W., Josse, B., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Stevenson, D. S., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G.: Analysis of present day and future OH and methane lifetime in the ACCMIP simulations, *Atmos. Chem. Phys.*, 13, 2563–2587, doi:10.5194/acp-13-2563-2013, 2013.
- Zindler, C., Bracher, A., Marandino, C. A., Taylor, B., Torrecilla, E., Kock, A., and Bange, H. W.: Sulphur compounds, methane, and phytoplankton: interactions along a north–south transit in the western Pacific Ocean, *Biogeosciences*, 10, 3297–3311, doi:10.5194/bg-10-3297-2013, 2013.