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On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere

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Abstract. Thousands of megatons natural and anthropogenic gases are released and subsequently removed from the troposphere each year. Photochemical reactions, initiated by hydroxyl (OH) radicals, oxidise most gases to products which are more easily removed by precipitation and dry deposition at the earth's surface. Since human-induced pollution emissions strongly affect OH formation and loss, large global changes in OH concentrations are possible. Global models and observations of trace gas distributions from global networks have been used to study geographical and temporal changes in tropospheric OH. Here we present a synopsis of recent studies, indicating that global mean OH has changed remarkably little in the past century, even though regional changes have probably been substantial. Globally, depletion of OH by reactive carbon gases has been compensated by increased OH formation by nitrogen oxides, an act of "inadvertent geo-engineering". However, OH analyses for the past 1–2 decades, partly based on methyl chloroform measurements, are inconclusive. Some work, assuming that methyl chloroform emissions have largely ceased, suggests a very strong downward global OH trend in the 1990s, inconsistent with modelling studies. The discrepancy could be much reduced by assuming continued small emissions of methyl chloroform. We recommend the continuation of high precision monitoring of this compound and improved analyses based on detailed meteorological-chemical models.

1 Introduction

The chemistry of OH in the troposphere is strongly linked to that of ozone (O_3) (Levy, 1971; Logan et al., 1981). The primary formation of OH is controlled by the solar ultraviolet (UV) radiation flux, dependent on the overhead O_3 column as well as the local O_3 and water vapour concentrations, according to the reactions 1–4 (Table 1). Photodissociation of O_3 at UV wavelengths yields electronically excited $O(^1D)$ atoms, which are largely quenched to the ground state $O(^3P)$ by air molecules in reaction 2, which subsequently recombine with O_2 to give ozone, hence establishing a null-cycle (reactions 1–3). Only a few percent of the $O(^1D)$ forms OH radicals, the exact amount being dependent on the humidity (reaction 4). Tropospheric OH concentrations are therefore highest in the tropics, where the solar zenith angle is smallest, the stratospheric ozone layer is thinnest, and the air humidity is highest (Fig. 1) (Logan et al., 1981; Crutzen, 1995; Spivakovsky et al., 2000; Lelieveld et al., 2002).

The high reactivity of OH is associated with a very short lifetime of about a second, so that its concentration is highly variable, depending both on source and sink gases and on ambient conditions, including cloudiness. Although OH can be measured quite accurately (Perner et al., 1987; Eisele et al., 1994; Hard et al., 1995; Brune et al., 1998; Heard and Pilling, 2003), its variability precludes that the spatially and temporally averaged OH-field, a measure for the atmospheric self-cleansing capacity, is determined from direct observations. An indirect method has therefore been developed, using long-term measurements of the tracer gas methyl chloroform (MCF), a compound which is largely removed from the atmosphere by OH and has only anthropogenic sources (Lovelock, 1977; Singh, 1977; Prinn et al., 1992). Thus a global diurnal mean OH concentration

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Table 1. Main atmospheric OH formation reactions (M represents air molecules N_2 and O_2).

No.	Reaction
1	$O_3+h\nu(\lambda<340\,\text{nm})\rightarrow O(^1D)+O_2$
2	$O(^1D)+M\rightarrow O(^3P)+M$
3	$O(^3P)+O_2(+M)\rightarrow O_3(+M)$
4	$O(^1D)+H_2O\rightarrow 2OH$
5	$O_3+HO_2\rightarrow 2O_2+OH$
6	$NO+HO_2\rightarrow NO_2+OH$

of $1.1\pm0.2\times10^6$ radicals/cm^3 has been derived (Prinn et al., 1995; Krol et al., 1998; Montzka et al., 2000), although some additional uncertainty may be caused by using different global weighting factors (Lawrence et al., 2001). By performing such calculations based on emissions and concentrations in the 1980s and 1990s, large OH changes in the past two decades have been inferred, also indicating much reduced global mean OH in the 1990s (Prinn et al., 2001; Krol and Lelieveld, 2003). If correct, changes of this magnitude could imply that the atmospheric self-cleansing capacity is very sensitive to perturbations. Here we provide a synthesis of recent research on this controversial issue, indicating that such changes cannot be reconciled with our present knowledge of global OH, while there is no compelling evidence to reject the present theory.

In Sect. 2 we review the main factors that determine the stability of the OH chemical system. Section 3 analyses our modelling results, based on Lelieveld et al. (2002), indicating regional OH redistributions and global mean OH changes in the 20th century. In Sect. 4 we analyse to what extent measurements from global networks are consistent with these modelling results in view of OH responses to tropospheric changes on a decadal time scale. Section 5 summarises our conclusions, highlights main uncertainties, and presents suggestions for future research.

2 Stability of tropospheric OH chemistry

A characteristic of chain reactions is that the radicals are recycled, and the length of the chain – i.e. propagation or termination – is of key importance. For example, the oxidation of carbon monoxide yields atomic hydrogen: $CO+OH\rightarrow CO_2+H$. In our O_2-rich troposphere the H atoms instantly form HO_2, after which the chain can either be terminated by forming a peroxide (e.g. H_2O_2) or propagated by radical recycling through secondary OH formation. The propagation involves either reaction 5 with O_3 – through which this OH precursor itself is lost– or the reaction 6 with nitrogen oxide (Table 1). The additional gain from reaction 6 is that NO_2 easily photodissociates, splitting off a ground state oxygen atom that forms ozone through reaction 3. In fact this is the central tropospheric O_3 production mechanism, and is also responsible for summer smog in polluted air. The crux is that in the presence of NO_x ($NO+NO_2$) ozone is formed and OH recycled, while in the absence of NO_x ozone is destroyed and the radical reaction chain terminates much more rapidly. Therefore, in the troposphere the NO_x abundance is usually the limiting factor in O_3 formation and OH recycling.

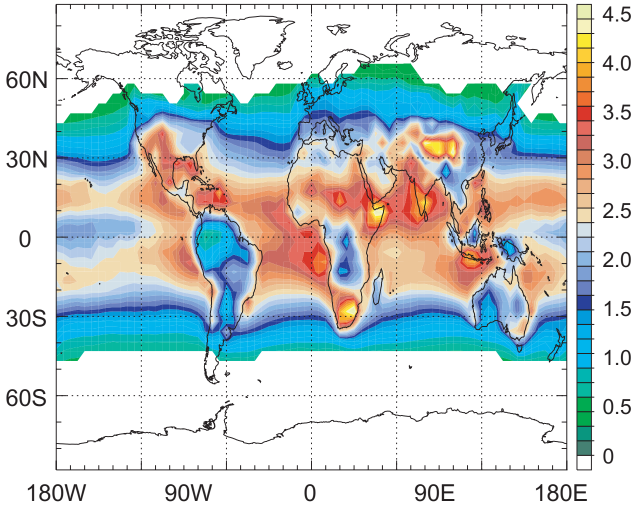

Fig. 1. Annual mean OH concentrations near the earth's surface, calculated with a chemistry-transport model (Lelieveld et al., 2002). The units are 10^6 radicals/cm^3. These results refer to OH in the boundary layer at low and middle latitudes where mean OH concentrations exceed 10^5 radicals/cm^3.

Thus we can distinguish two regimes: first, an NO_x-enriched environment where O_3 is formed and OH recycled, and second an NO_x-depleted environment where O_3 is destroyed and OH runs down (Crutzen, 1979). One can imagine that a perturbation of the OH chemical system, applied through an increase in reactive carbon compounds such as CO or CH_4, is not likely to be amplified in the NO_x-enriched conditions. In this case the OH radicals consumed in the initial reaction are recycled, and more radicals are produced through the enhanced O_3 formation. In the NO_x-depleted system, on the other hand, an increase in reactive carbon enhances OH loss, so that the lifetimes of the carbon compounds increase, and the system can end in catastrophic OH loss. Theoretical studies have shown that the nonlinear dynamics of atmospheric photochemistry allow multiple steady states and even oscillatory behaviour, depending on the timescales and the NO_x concentrations considered (Stewart, 1995; Poppe and Lustveld, 1996; Krol and Poppe, 1998).

The extent to which the system is sensitive to perturbations can be illustrated by considering the oxidation power (G) of an air parcel, defined as the rate at which OH is produced (gross OH production), i.e. the sum of primary (P)

and secondary (S) OH formation. In the troposphere, P is dominated by reaction 4, and S by reactions 5, 6 and the photodissociation of peroxides. As shown by Lelieveld et al. (2002), the relation of the oxidation power G to primary OH formation P can be written as:

$$G = P + S = \frac{P}{1 - r} \tag{1}$$

and r=1−P/G, called the OH recycling probability; r represents the efficiency at which the OH radicals are recycled after their initial loss in an oxidation reaction. Figure 2 shows the global mean tropospheric OH recycling in which P=92 Tmol/yr, S=96 Tmol/yr and thus G=188 Tmol/yr. Consequently, the OH recycling probability r=1−92/188≈0.5. If the system were dominated by primary OH formation, for example, if tropospheric O_3 were dependent only on transport from the stratosphere and $r \rightarrow 0$, it would be highly sensitive to perturbations. In the other extreme, if secondary OH formation were dominant and $r \rightarrow 1$, the system could become autocatalytic with runaway oxidant formation. Since these extreme conditions are not desirable for life on earth, the intermediate value of r≈0.5 seems favourable.

3 Global OH redistribution

The above argument offers some reassurance that the self-cleansing capacity of the atmosphere is not at risk. However, there is a complication. Even though the troposphere is well-mixed on a time scale of a few months hemispherically and over a year globally, we may question if the global OH chemistry can be represented as one single reaction vessel. In regions where intensive fossil fuel use leads to large NO_x emissions, e.g. in Europe and the USA, strong oxidant formation is typically associated with a relatively high value of r>0.65 (Lelieveld et al., 2002). This indicates, for example, that the OH concentration is relatively insensitive to increases of reactive carbon compounds. Over the tropical and subtropical oceans, on the other hand, for which r<0.35, OH is much more sensitive to these perturbations.

In the marine environment NO_x emissions are generally low or absent, and O_3 loss dominates O_3 formation. Therefore the OH chemical system is strongly dependent on O_3 transport from the stratosphere and on transport of pollutant O_3 and NO_x reservoir species from the continents. An important NO_x reservoir gas is peroxyacetyl nitrate (PAN), which is thermally labile. PAN can travel over large distances in the cold upper troposphere, and releases the NO_x in warmer air near the surface (Singh and Salas, 1983). The lifetime of NO_x itself is only about one day, so that its transport potential is limited. In contrast, the lifetime of O_3 is typically a few weeks to a few months, therefore, O_3 can be effectively transported over large distances. Furthermore, carbon compounds such as CO and CH_4 have lifetimes of a few months to nearly a decade, respectively, so that the continental emissions easily reach the marine troposphere.

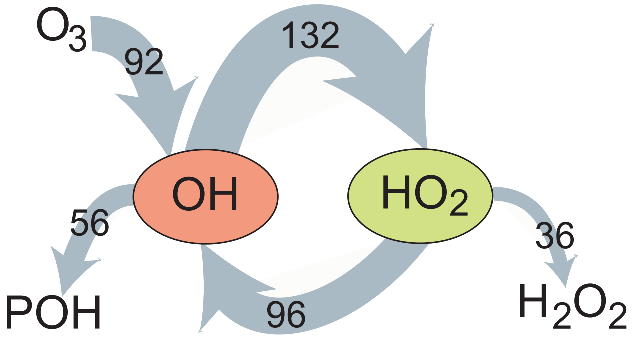

Fig. 2. Global mean OH recycling in the troposphere in Tmol/yr, calculated with a chemistry-transport model (Lelieveld et al., 2002). POH means partly oxidised hydrocarbons, a term associated with substantial uncertainty.

Global emission inventories have been compiled of the main compounds involved in tropospheric O_3 and OH chemistry, which show the dominant role of human-induced sources (Van Aardenne et al., 2001; Brasseur et al., 2003). It should be noted that in particular natural sources of non-methane hydrocarbons are very uncertain, and that recent in-canopy measurements suggest that forest emissions may have been substantially underestimated, which could have important consequences for analyses of atmospheric oxidation processes (Karl et al., 2004). The estimated anthropogenic fraction of the global annual source of reactive carbon (more than two billion tons of CO, CH_4 and non-methane hydrocarbons) and of reactive nitrogen (40–50 million tons of NO_x), is about 70–75%, to which fossil fuel use and biomass burning contribute most. Considering the different transport potentials of these compounds and the uneven sensitivities of the OH chemistry, it is obvious that these large anthropogenic perturbations have global though regionally diverse consequences. Our model simulations indicate that a large-scale OH re-distribution has taken place in the past century, whereby OH has substantially increased over the polluted continents and decreased over the oceans (Lelieveld et al., 2002). Remarkably, the model results show that the global average OH concentration has remained within about 10% of its pre-industrial value, because the compounds which deplete OH, namely CO and CH_4, and the nitrogen oxides that enhance O_3 and OH recycling, have increased in parallel (Isaksen and Hov, 1987; Prather, 1994; Lelieveld and Van Dorland, 1995; Wang and Jacob, 1998). Although regional perturbations can lead to strong OH changes, it looks as if the global system responds almost linearly owing to large-scale transport and mixing. Regional differences are partly compensated by the transport of oxidants, mostly ozone, PAN and to a lesser extent NO_x from polluted to pristine regions, i.e. from the continents to the oceans.

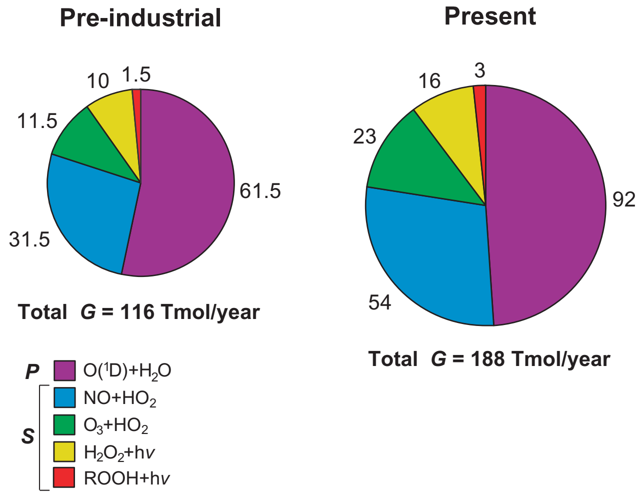

Fig. 3. Model calculated annual OH formation rates (Tmol/year) through the main chemical pathways, based on present-day and pre-industrial emissions of natural and anthropogenic origin.

Model calculations of global OH formation rates for present-day and pre-industrial emission scenarios indicate that the global oxidation power G has increased from 116 to 188 Tmol/year, i.e. it has increased by about 60% in the past century (Fig. 3). This increase has offset the additional OH loss from increasing CO and CH_4. Observations unambiguously demonstrate that CO and CH_4 concentrations have grown by at least a factor of two in the past century (Brasseur et al., 2003). The model results indicate that these large perturbations have not had major consequences for global mean OH, i.e. the overall tropospheric self-cleansing capacity. Moreover, the partitioning between primary and secondary OH formation and thus the mean value of $r \approx 0.5$ has remained approximately constant. Interestingly, we may conclude that the global troposphere shows some characteristics of a well-mixed reaction vessel, at least to the extent that regional differences have been partly compensated. However, this holds no guarantee for future atmospheric composition changes (Prinn, 2003), especially if larger parts of the globe would change into either high-r or low-r regions depending on the mix of reactive nitrogen and carbon emissions.

4 Inter-annual variability and trend

Next we consider whether this theoretical argument is consistent with experimental evidence. We know from direct observations that a number of the main factors that influence OH have changed during recent decades (Brasseur et al., 2003). Table 2 presents a summary of these system forcings, whereby the responses assume that each forcing takes place in isolation. The response to a change in non-methane hydrocarbons (NMHCs) is as yet unclear, especially because the sources and effects of partly oxidised hydrocarbons are poorly known (Karl et al., 2004). For example, NMHC oxidation can locally reduce OH and form products that release OH during transport. In addition, effects of aerosols and clouds are quite uncertain, associated with multiphase chemistry and the scattering and absorption of solar radiation. Obviously the overall response is a combination of partly compensating effects. We can nevertheless assume that if the global OH chemical system were unstable OH would exhibit large inter-annual and long-term variability, because the controlling factors vary on a wide range of scales. Measurements of relatively long-lived tracers which are removed by OH can provide such information.

Methane has a mean lifetime of about 9 years; it is therefore globally mixed even though its sources are mostly located in the northern hemisphere (NH). Its seasonal cycle is to a large degree determined by that of OH, especially in the southern hemisphere (SH). Model simulations can reproduce the seasonal inter-hemispheric CH_4 asymmetry and the slightly larger CH_4 growth in the NH compared to the SH in the past century, consistent with analyses of Greenland and Antarctic ice cores (Houweling et al., 2000). Measurements from a global network indicate an inter-annual CH_4 lifetime variability smaller than 1–2% (Dlugokencky et al., 1998), which can be explained by global OH changes caused by the main factors listed in Table 2, as represented by models (Dentener et al., 2003). Principal component analysis has shown that stratospheric O_3 loss, leading to enhanced UV penetration into the troposphere, and water vapour changes – e.g. in response to global warming – significantly affect primary OH formation. The variability in emissions and transport of precursor gases plays an important role as well. The inter-annual variability of the global OH loss rate appears to be dominated by the irregular meteorological conditions that affect the transport of CO. The Mt Pinatubo eruption in 1991 turned out to be an interesting "natural experiment" as it caused a ∼2 year increase of stratospheric O_3 loss, which can clearly be discerned in the CH_4 record (Dentener et al., 2003). It has also been shown that the signal of the solar cycle, through the effect on stratospheric O_3 and tropospheric UV radiation, can be retrieved from the inter-decadal variability of CH_4. Chemistry-transport modelling can thus reproduce these factors.

A further test of the theory may be obtained from the analysis of methyl chloroform (MCF) measurements. This highly volatile substance with the official name 1,1,1-trichloroethane, used as an industrial solvent, has escaped to the atmosphere in well-known quantities (McCulloch and Midgley, 2001), and it is the most suited among a number of anthropogenic tracers to constrain global OH budget calculations (Spivakovsky et al., 2000). MCF has been measured at background stations since 1978, showing a steep increase until it reached a maximum in 1992, after which it declined rapidly because it has been phased out under the Montreal Protocol to protect the ozone layer (Prinn et al., 1995, 2001;

Table 2. Major influences on the OH concentration in the troposphere.

Forcing	Mechanism	Response
CH_4↑	$CH_4+OH\rightarrow$products	OH↓
CO↑	$CO+OH\rightarrow$products	OH↓
NO_x↑	O_3 formation, OH recycling	OH↑
NMHCs↑	NMHC oxidation→products	OH ?
Aerosols↑	Sunlight extinction; heterogeneous chemistry	OH ?
Clouds↑	Sunlight extinction; multiphase chemistry	OH ?
Rain rate↑	H_2O_2 deposition↑	OH↓
H_2O↑	$H_2O+O(^1D)\rightarrow 2OH$	OH↑
CFCs↑	stratospheric O_3↓, tropospheric UV↑	OH↑

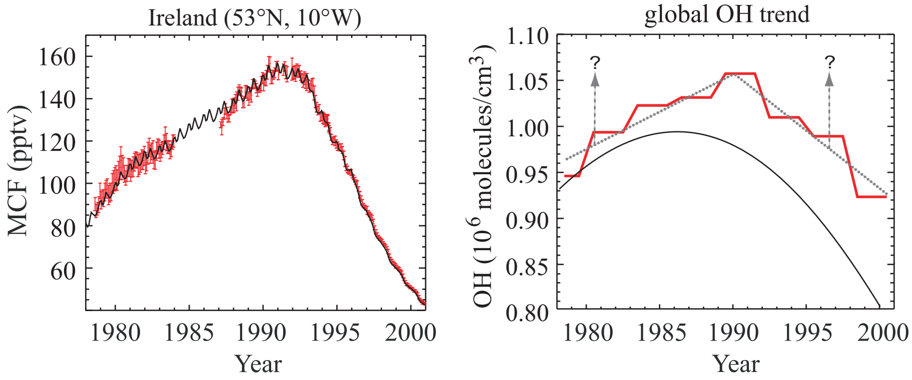

Fig. 4. Comparison of MCF and OH trends since 1978. Left: methyl chloroform measurements (red) at a background station (Prinn et al., 2001) and model-optimized MCF (black). Right: global OH trend derived from MCF data for 3-year periods (Krol and Lelieveld, 2003). The dotted lines indicate the mean OH trends before and after 1990. The black solid line indicates the global OH trend derived by Prinn et al. (2001).

Montzka et al., 2000). The lifetime of MCF against destruction by OH is about 5.5 years, and it has minor additional sinks by dissolution in the oceans and photodissociation in the stratosphere (where it releases O_3-destroying chlorine). Because of the relatively slow response time of the ocean and stratospheric MCF reservoirs as compared to the rapid MCF decline in the troposphere, the importance of these minor additional sinks decreases with time, which needs to be accounted for in studies of the global OH trend (Krol and Lelieveld, 2003).

Several such studies have been performed based on different methods including inverse modelling (Prinn et al., 1995, 2001; Krol et al., 1998, 2003; Montzka et al., 2000). Figure 4 (left panel) shows MCF measurements from Mace Head on the west coast of Ireland (Prinn et al., 2001), the model-optimised MCF concentrations, and the inferred OH concentrations (right panel) (Krol and Lelieveld, 2003). The global MCF-derived OH trend is shown for 3-year periods. Figure 4 also shows the global OH trend derived by Prinn et al. (2001); this turns down earlier and more strongly in the 1990s, largely because the MCF transport processes, e.g. between the troposphere and stratosphere, have been calculated with a coarse model, as discussed by Krol and Lelieveld (2003). Whether or not these strong OH trends, as indicated in Fig. 4, are real appears to be largely dependent on the accuracy at which the MCF emissions have been estimated.

These large changes of 5–10% over decadal periods (and even larger changes according to Prinn et al., 2001) are difficult to reconcile with our present knowledge of the major factors that influence global OH, as summarised in Table 2. In fact, if the observed changes in these factors could lead to decadal OH changes of 5–10% or more, the OH chemical system could be unstable, because the response may be larger than the forcing. Closer inspection of Fig. 4, however, reveals that the MCF and OH tendencies since 1978 are very similar, with a trend break around 1990, which is surprising, since MCF has an insignificant effect on global OH. The question really is how accurately the emissions are known. The widely used inventory indicates that the total MCF emissions increased from about 5 Gg/yr in the 1950s to 718±17.1 Gg/yr in 1990, dropping to 19.7±0.7 Gg/yr in 2000 (McCulloch and Midgley, 2001; Prinn et al., 2001).

A key to this puzzle may be the temporal distribution of the MCF emissions. Aircraft and ground-based measurements in 2000 and 2001 showed higher MCF concentrations than expected over eastern and southern Europe, up to about 60 pptv in 2000 and 2001, which points to substantial unreported emissions (Krol et al., 2003; Gros et al., 2003). Recent analyses are contradictory, however, and only confirm smaller MCF emissions from Europe, although still higher than assumed by Prinn et al. (2001) (S. Reimann, personal communication). Ground-based measurements in the USA in the period 1996–2002 and aircraft measurements downwind of China in 2001 also indicate continued MCF emissions (Barnes et al., 2003; Millet and Goldstein, 2004; Blake et al., 2003). On the other hand, Palmer et al. (2003) infer that the amount of MCF released from East Asia is consistent with the estimate of McCulloch and Midgley (2001). Furthermore, Wennberg et al. (2004) infer that the high latitude oceans have recently become an MCF source rather than a sink. Taking this into account in the inverse calculations of OH would lead to a higher global mean OH and a reduction of the negative trend in the 1990s.

In view of this conflicting information, the only conclusion that can presently been drawn is that the global MCF emissions in the 1990s were probably higher than assumed by McCulloch and Midgley (2001), whereas a quantitative evaluation is not yet possible. It is conceivable that the MCF source inventory has underestimated the effect of MCF stockpiling prompted by the Montreal Protocol. For example, if we assume that about 0.5–1% (65 Gg) of the total MCF emission after 1980 was delayed from the 1980s to the 1990s, both the strong upward and downward OH tendencies for these periods, respectively, vanish, as indicated by the arrows in Fig. 4. This would be in better agreement with model studies that do not reproduce the OH decline after 1990, but rather predict a gradual upward OH tendency since about 1980 caused by a combination of pollution emissions, stratospheric ozone depletion, and increasing atmospheric water vapour associated with global warming (Krol et al., 1998; Karlsdòttir and Isaksen, 2000; Dentener et al., 2003). This contrasts with the strong inter-annual and inter-decadal variability derived by Prinn et al. (2001), including a strong downward OH trend in the 1990s, partly also derived by Krol and Lelieveld (2003). This discrepancy can only be resolved if the accuracy of the MCF emissions is improved, and by using state-of-the-art chemistry-transport models that account for the inter-annual variability of OH precursor emissions and meteorological processes, including stratosphere-troposphere and ocean-atmosphere exchanges.

5 Central issues and future research

It is not merely an academic question whether OH concentrations have changed, because OH controls the lifetime of trace constituents and their impact on air quality and climate. It is difficult, however, to quantitatively determine the large scale OH distribution and in particular the variability and long-term changes in this distribution. In our view, the analyses of long-lived tracers such as CH_4 and MCF do not support large global inter-annual or inter-decadal OH changes, while some studies indicate an upward tendency of OH since about 1980. Our synopsis of recent MCF analyses shows that the results are ambiguous so that additional studies with improved emission estimates and a more detailed representation of short- and long-term meteorological variability are required. Furthermore, continued high precision MCF measurements in future, when illegal or unaccounted emissions will vanish, will be of great use to global OH analyses.

One may also consider using new chlorofluorocarbon substitutes that react with OH, since the observational database for these gases is growing (Huang and Prinn, 2002). It has furthermore been proposed to apply dedicated tracers, such as deuterated halocarbons, solely produced and released to monitor OH (Jöckel et al., 2003). Furthermore, the use of satellite measurements, for example, by assimilation of OH precursor data in models, may help to constrain the global OH budget, although it will take time before the data sets cover periods over which trends can be calculated.

It has been shown in several studies that comprehensive physical-chemical measurements can constrain the local radical budget in selected air masses under different conditions, which provides some confidence that the main controlling factors are known, although some chemical pathways involving multiphase processes and a host of NMHC compounds e.g. in polluted air remain difficult to quantify (Jaeglé et al., 2001; Mauldin et al., 2001; Tan et al., 2001; Mihelcic et al., 2003; Cantrell et al., 2003). Such comprehensive measurements are nevertheless scarce in the tropical troposphere for which models predict large differences between continental and marine conditions. Figure 1 shows large zonal and meridional OH gradients between the tropical oceans and forests, especially near South-America, which provides excellent conditions to test the theory. In particular the emissions of natural NMHCs and partly oxidised hydrocarbons from forests and oceans, lightning produced NO_x, as well as interactions with clouds and pollutants (including aerosols) and their transport are quite uncertain, thus requiring laboratory and field measurement studies.

Model simulations indicate that in the past century a large-scale OH redistribution between the continents and the oceans has taken place, with strong increases over polluted regions and decreases in the marine troposphere. Measurements show that OH concentrations can indeed be very high in NO_x-enriched air, common in the densely populated parts of the continents, and that OH concentrations are much lower in more pristine environments. It seems fortuitous that the global mean OH concentration may have changed relatively little in the past century in spite of large regional pollution effects. The simultaneous pollution emissions of reactive carbon and nitrogen species and their relatively rapid mixing and transport in the turbulent troposphere have prevented large global OH changes. We would call this "inadvertent geo-engineering". Moreover, this compensation may have concealed the true sensitivity of the OH chemical system, so that responses to future perturbations are uncertain.

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