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The impact of anthropogenic chlorine, stratospheric ozone change and chemical feedbacks on stratospheric water

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Abstract

Mixing ratios of water (H_2O) in the stratosphere appear to increase due to increased input of H_2O and methane (CH_4) from the troposphere and due to intensified oxidation of CH_4 in the stratosphere, but the underlying mechanisms are not yet understood. Here we identify and quantify three chemical mechanisms which must have led to more efficient oxidation of CH_4 over the past several decades: 1) The increase in stratospheric chlorine levels due to anthropogenic CFC emissions, 2) the thinning of the stratospheric ozone column and 3) enhanced OH levels in the stratosphere due to increasing H_2O levels themselves. In combination with the increase in tropospheric CH_4 mixing ratios and with solar cycle related variations of upper stratospheric ozone, these effects can explain about 50% of the additional conversion of CH_4 to H_2O as observed throughout the stratosphere. The relative contributions from the individual processes have varied over the past decades.

1. Introduction

The observed increase of water vapor mixing ratios in the stratosphere (Oltmans and Hofmann, 1995; Oltmans et al., 2000; SPARC, 2000; Rosenlof et al., 2001) has received considerable attention because of its importance for the earth's radiative balance (Forster and Shine, 2002) and stratospheric microphysical conditions, which affect ozone destruction (Kirk-Davidoff et al., 1999; Tabazadeh et al., 2000). Understanding this increase represents one of the great challenges in present atmospheric research. The collective evidence from numerous in situ and remote sensing measurement series of stratospheric water vapor suggests a positive trend of roughly 0.45%/yr (Rosenlof et al., 2001), which may have persisted for about 45 years, if the earliest measurements are reliable. Additional insight can be gained from measurements of CH_4, because CH_4 oxidation is the only substantial in situ source of water in the stratosphere. This means that once an air parcel has entered the stratosphere, its H_2O

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mixing ratio gradually increases as CH_4 is oxidized. Since two water molecules are formed for each CH_4 molecule destroyed, the quantity $H_2O + 2\times CH_4$ is conserved in the stratosphere, if the mixing ratio of the third hydrogen reservoir, H_2, does not change (Jones et al., 1986).

Global remote sensing observations of H_2O and CH_4 from the Halogen Occultation Experiment (HALOE) from 1992 to 1997 (Randel et al., 1999) revealed two separate features at different altitudes in the stratosphere: 1) a uniform positive trend of $H_2O + 2\times CH_4$ throughout the stratosphere above 25 km, that is likely due to increasing input of water from the troposphere (Zhou et al., 2001; Rosenlof, 2002; Sherwood, 2002) and 2) superimposed a H_2O trend which gradually increases with altitude, accompanied by a gradually decreasing trend in methane mixing ratios, which even turns negative at altitudes above about 30 km (Fig. 6 in Randel et al., 1999). Thus, although CH_4 mixing ratios were increasing in the troposphere (Blake and Rowland, 1988; Dlugokencky et al., 1994) they were actually decreasing in the middle and upper stratosphere. This observation indicates that the efficiency of the conversion of CH_4 into H_2O has increased over the considered time period, however, the reasons for this more efficient CH_4 oxidation are not yet understood. Rosenlof (2002) recently suggested that changes in the residual circulation can lead to increased residence times of CH_4 in the stratosphere and thus may contribute to an intensified conversion to H_2O. In addition to this dynamical mechanism, we show here that an increased oxidation of CH_4 by Cl, $O(^1D)$ and OH radicals must have caused a more efficient conversion of CH_4 to H_2O in the past decades, and that this mechanism has contributed significantly to the observed H_2O trends in the middle and upper stratosphere.

2. Stratospheric in situ production of H_2O

The relative strengths of the three CH_4 sink processes, reaction with Cl, $O(^1D)$ and OH, can be obtained from CH_4 isotope measurements, because all three reactions are associated with different isotope fractionations. Recent measurements of the heavy

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isotope content of stratospheric CH_4 are reproduced well in atmospheric models when the relative share of the Cl-based stratospheric CH_4 sink is 20 to 35% (Saueressig et al., 2001; McCarthy et al., 2003; Rice et al., 2003). Thus, the reaction with Cl is an important sink of CH_4 in the present day stratosphere. The history of the atmospheric chlorine burden and its increase due to anthropogenic CFC emissions in the second half of the 20th century is well established (Butler et al., 1999; WMO, 2003). What has never been assessed quantitatively, however, is the effect of the strong increase in chlorine on the destruction rate of CH_4 in the stratosphere: By drastically increasing the Cl-based sink of stratospheric CH_4, the conversion of CH_4 to H_2O will become more efficient, and a simultaneous increase in stratospheric H_2O is inevitable.

The most important consequence of the CFC emissions was the chlorine catalyzed destruction of ozone in the stratosphere. In addition to the well-known dramatic destruction of stratospheric ozone in polar spring, publicly known as the "ozone hole", ozone has also been reduced by anthropogenic chlorine on a global scale. Observations between 1979 and 1999 show that the decline of O_3 is altitude dependent and amounts to 3–6% per decade in the 40–50 km altitude range (WMO, 2003). In addition to destruction by Cl, upper stratospheric ozone is also affected by the solar cycle (WMO, 2003). A global ozone decrease in the upper stratosphere causes a further chemical feedback on stratospheric water vapor. The ozone photolysis rate $J(O_3)$ and thus the production rate of $O(^1D)$ critically depends on the ozone column above the photolysis region. The thinning of the ozone column above increases the actinic flux available for the photochemistry of O_3 at a certain altitude and thus increases the $O(^1D)$ production rate. More $O(^1D)$ production means increased destruction of CH_4 and thus enhanced production of H_2O. In addition, since OH in the stratosphere is primarily formed via

$$O(^1D) + H_2O \rightarrow 2OH \quad (1)$$

a higher $O(^1D)$ concentration also means more OH production. Hence, the thinning of the upper stratospheric ozone column must have caused an increase of $O(^1D)$ and OH

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levels and thereby a more efficient conversion of CH_4 to H_2O.

According to reaction (1) the increase of water vapor levels in the stratosphere itself will also lead to a higher OH production rate. Thus both, the additional H_2O input from the troposphere, as well as the additional H_2O from more efficient CH_4 oxidation as just described, cause higher OH concentrations and in turn an intensified production of H_2O from CH_4.

In combination, the increase in anthropogenic CFC emissions, the variations in stratospheric ozone and the increased input of tropospheric water into the stratosphere must have caused a more efficient oxidation of $CH_4$and thus production of H_2O in the stratosphere. We note that there are additional second order effects, e.g. the Cl- and $O(^1D)$-initiated removal of CH_4 will produce OH radicals further along the CH_4 oxidation sequence, which are not discussed in detail here.

3. Model calculations

We have carried out stratospheric model calculations to investigate these three effects in detail. Atmospheric models are available at various levels of complexity ranging from box models to high resolution 3-D models. Each of these model types has its particular strengths and weaknesses. For our study we use a chemical box model to focus on the chemical mechanisms that are put forward here. This model neglects atmospheric mixing effects but allows to correctly describe the age of air in an air parcel rising in the stratosphere in the tropics. Further, we have carried out simulations with a two-dimensional model to investigate the impact of mixing and to examine the latitude dependence of the results. We note that 2-D (and 3-D) models generally underestimate the mean age of stratospheric air (Hall et al., 1999), i.e. they transport air too quickly through the stratosphere. Nevertheless, the results from the box model and 2-D model calculations, each having inherent deficiencies, provide a consistent picture, which gives us confidence that the results presented here are robust and are not dependent on a particular model.

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Our box model consists of the chemistry module of the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002). Simulations are performed along an idealized trajectory for a single air parcel that rises from the tropical tropopause (15° N) to 1 hPa within 4 years, as deduced and extrapolated from observations of water vapor variations ascending in the tropical stratosphere (Mote et al., 1996; Rosenlof, 2002). As mentioned above, atmospheric mixing is neglected in such box model calculations. This leads to altitude profiles of CH_4 mixing ratios that decrease too slowly in the lower stratosphere below about 10 hPa and too quickly above, when compared to stratospheric conditions, where mixing decreases the meridional gradients. Nevertheless, the total removal of CH_4 in the model is realistic, and half of the tropospheric CH_4 is decomposed at about 3 hPa, which is comparable to HALOE CH_4 observations.

Along the path of the considered air parcel the complete stratospheric photochemistry with 98 chemical and 36 photolysis reactions is simulated, including CH_4 oxidation and decomposition of CFCs and N_2O. Typical monthly temperature changes are included in the idealized trajectories. Abundances of the radical species Cl, OH and $O(^1D)$ are calculated from their precursors (e.g. CFCs, O_3 or H_2O itself), using recommended photolysis and chemical rate coefficients (Sander et al., 2000). The air parcel is initialized with a chemical composition taken from simulations with the Mainz photochemical 2-D model (Gidel et al., 1983; Grooß, 1996). The underlying boundary conditions for all box and 2-D model simulations in this study are taken from the WMO scenarios (WMO, 1999; WMO, 2003). Based on these scenarios and the observed trends of water input from the troposphere (SPARC, 2000; Rosenlof et al., 2001) we then varied for the considered time periods the initial CFC, H_2O and CH_4 content of the air parcel, as well as the ozone profile that is used in the radiative transfer code to determine the photolysis frequencies, to study the effects on upper stratospheric water. This means that the temporal trends in radical abundances are wherever available based on observed trends of the precursor molecules (we note that direct observations of trends in radical concentrations do not exist).

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4. Results

In Fig. 1a, we show the simulated H_2O and CH_4 trends for the 1980s, a period with strongly increasing atmospheric CH_4 and CFC levels. This leads to a substantial stratospheric water increase of up to 0.27 ppm/decade at 1 hPa, which is more than just the transfer of the tropospheric CH_4 trend shown by the green line in Fig. 1a. The reduction and even reversal of the CH_4 trend at higher altitudes clearly illustrates that the oxidation of CH_4 has become more efficient due to the anthropogenic CFC emissions. When we also include a decadal increase of water vapor input from the tropopause of 0.5 ppm, which equals the average trends from all available measurements (Rosenlof et al., 2001), the corresponding increase in OH results in further conversion of CH_4 to H_2O. Finally, a reduction of the upper stratospheric partial ozone column by 5% in the 1–10 hPa region (this value is representative for the 1980s (WMO, 2003)) also leads to more efficient oxidation of CH_4 to H_2O, augmenting the trend due to increased Cl and H_2O levels. Thus, as argued above, all three chemical effects cause an intensified CH_4 oxidation in the stratosphere, leading to a significant increase of upper stratospheric water levels. Since many of the chemical reaction rate coefficients are temperature dependent and stratospheric temperatures have changed over the periods considered below, we carried out sensitivity tests to examine the effect of changing temperatures on our results. For a trend of 2 K/decade, which is at the upper limit of observational values (WMO, 2003), the effect of the temperature changes was about 10 ppb/decade, i.e. at least one order of magnitude smaller than the combined chemical effects.

The box model results are corroborated by 2-D model calculations (Fig. 2). The general trends are similar to the box model results: CH_4 is more efficiently oxidized to H_2O throughout the middle and upper stratosphere when its removal rate is increased by the three chemical mechanisms. The total trends are slightly smaller, and so CH_4 trends change sign at an altitude slightly higher than deduced from the box model simulations. We note that in the 2-D model only the effects due to the increase of CH_4 and Cl levels (and the corresponding ozone depletion, which is calculated self-consistently) are con-

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sidered; solar cycle effects on O_3 and the increase of H_2O input from the troposphere are not included. Based on the box model results, including the latter effect would bring the results from the two models into even better agreement. The 2-D simulations also show that the modeled trends depend only moderately on latitude, which confirms that the box model calculations at 15° N can be taken as representative for a greater latitude range.

Global satellite observations of stratospheric water vapor from the HALOE instrument became available in late 1991. We now consider the period 1992 to 1997, for which a strong increase in upper stratospheric H_2O trends with altitude was reported based on HALOE data (Randel et al., 1999). The period of 1992 to 1997 was a characterized by a decrease in the tropospheric CH_4 growth rate (Dlugokencky et al., 1994) and the decline in CFC emissions as a consequence of the Montreal protocol (WMO, 2003). Also, global ozone observations from the HALOE and SAGE II instruments show a strong decline in upper stratospheric ozone. This is likely a solar cycle effect (WMO, 2003) since it happened during the declining phase of the solar cycle, but it has also been associated with the eruption of Mount Pinatubo in 1991 (Randel et al., 1999). For our simulations we use the annual average of HALOE O_3 measurements at 15±5° N, the latitude of our box model simulation, from 1992 and 1997, which show a decrease of 3–4% between 5 and 0.1 hPa. The results show that H_2O production from the increase of CH_4 and CFCs alone was much smaller during that period than during the 1980s (Fig. 1b). However, the large change in the O_3 column more than compensates for the smaller chlorine and CH_4 increase, and the additional oxidation of CH_4 is even stronger than in the 1980s. Thus, the altitude dependence of the trends from 1992 to 1997 which were observed in the stratosphere (Randel et al., 1999) is reproduced in the model results in Fig. 1b: CH_4 trends decline and even turn negative at high altitudes and H_2O trends slowly increase with altitude. The chemical changes discussed here can account for about 50% of the observed atmospheric CH_4 trends (Fig. 1b). The most important contributor to the trends from 1992 to 1997 is the decline in upper stratospheric ozone. This also implies that the HALOE derived H_2O trend dur-

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ing the early 1990s was biased by solar cycle related variations in atmospheric ozone changes in a manner not recognized previously. This is supported by investigations of longer HALOE time series, which generally show smaller temporal trends (Rosenlof, 2002).

Over the following 5 years, 1997–2002, the upper stratospheric H_2O increase as observed with HALOE was negligible (Rosenlof, 2002; Nedoluha et al., 2003). We also investigated the chemical changes for this period. Since 1997–2002 was an increasing phase of the 11 year solar cycle, upper stratospheric O_3 increased and we use an increase of 1–3% between 5 and 0.1 hPa, derived from the HALOE data. Owing to the regulations under the Montreal protocol, the chlorine loading was almost unchanged. Figure 1c shows that there is indeed no effect due to CFC emissions, but the global increase of tropospheric CH_4 mixing ratios still caused H_2O mixing ratios to increase in the upper stratosphere. This is augmented by increased water input from the troposphere, while the increase of the O_3 column now actually diminishes the increase of H_2O. In combination, all effects together produce only a small increase of up to 80 ppb/decade, thus 40 ppb over the 5 year period. This is less than in the earlier periods, in agreement with the observations, which do not show a significant trend for 1997–2002.

5. Future development

The above model results show that anthropogenic CFC emissions, the resulting thinning of the upper stratospheric ozone column as well as the chemical effect of increased water input from the troposphere have led to a significant increase in middle and upper stratospheric water since the 1980s. Further, solar cycle effects have a strong impact, and have partly masked the long-term trends in the first decade of global satellite observations. It is predicted that with the regulations of CFCs under the Montreal protocol, chlorine levels in the stratosphere will decrease further in the future, and that the ozone depletion will slow down and will eventually reverse (WMO,

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1999; WMO, 2003). Figure 3 shows box model predictions for upper stratospheric water trends from 2000 to 2050. In these calculations we have assumed future stratospheric chlorine levels based on the WMO halocarbon baseline scenario (Table 4B-3 in WMO, 2003). Also tropospheric CH_4 mixing ratios follow the WMO baseline scenario (Table 12.2 in WMO, 1999), i.e. they increase to 2000 ppb in the year 2050. The ozone profiles used come from a 2-D model simulation driven by these scenarios. The results show that primarily the assumed continuing increase of atmospheric CH_4 will cause upper stratospheric water levels to increase further (Fig. 2). In contrast to the conditions in the 1980s, the decline in chlorine and the recovery of stratospheric ozone will reduce the increase of H_2O, i.e. they cause a less efficient conversion of CH_4 to H_2O in the future. Since the future CH_4 increase is difficult to predict (Simpson et al., 2002), this important contribution to the H_2O trends is uncertain: The orange lines show the results employing alternatively the WMO scenario A2 (Table 4B-3 in WMO, 2003) with an increase of tropospheric CH_4 to 2562 ppb in 2050. Also, the future development of the input of tropospheric water into the stratosphere is very speculative and is therefore not included in the prediction, and neither is the possible impact of a future hydrogen economy as a potential additional source of stratospheric water, as discussed recently (Tromp et al., 2003).

6. Conclusions

Increases in the abundance of stratospheric abundances of Cl, $O(^1D)$ and OH due to anthropogenic CFC emissions, the thinning of the stratospheric ozone column and increasing input of water from the troposphere have led to enhanced chemical conversion of CH_4 to H_2O in the past decades. Clearly, the more efficient oxidation of CH_4 as described in this paper can not explain the observed increase in the quantity $H_2O + 2\times CH_4$ in the stratosphere. Likewise, the chemical mechanisms are unlikely to cause large interannual and spatial variability in the trends, and we expect that this variability may be caused by dynamical changes (Considine et al., 2001; Rosenlof, 2002).

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Nevertheless, the comparison of model simulations and observations indicates that approximately 50% of the observed enhanced oxidation of CH_4 in the stratosphere can be attributed to chemical changes. Thus, these chemical changes, which are based on reliable atmospheric observations and well-established chemical reaction mechanisms, have to be taken into account when stratospheric water vapor trends are analyzed. We conclude that this chemical mechanism constitutes an important contribution to the explanation of the total stratospheric water trends.

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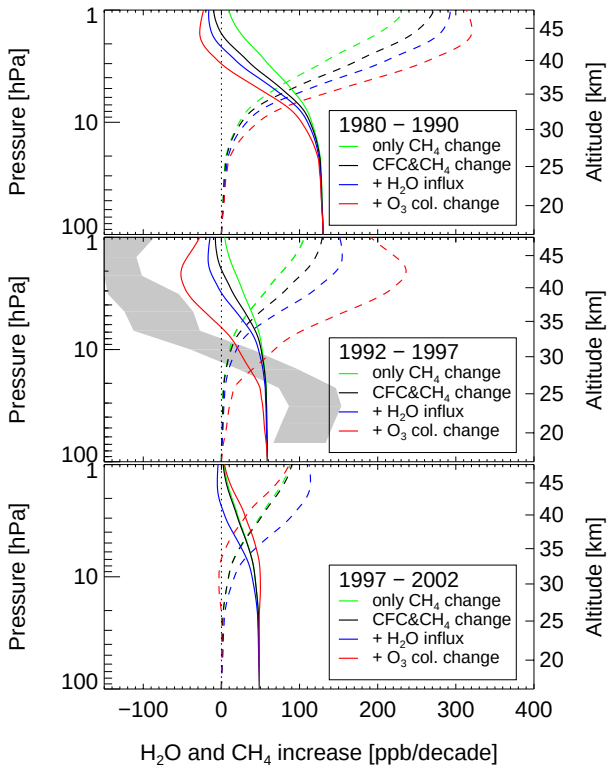

Fig. 1. Box model calculations illustrating the effect of increasing CH_4 and CFC levels in the atmosphere, increasing input of water from the troposphere to the stratosphere and a change of the upper stratospheric ozone column on water levels in the stratosphere for the period of the 1980s **(a)**, 1992–1997 **(b)**, and 1997–2002 **(c)**. Solid lines show the CH_4 trends and dashed lines the H_2O trends over the respective periods. The additional H_2O input from the troposphere of 500 ppb/decade (for the blue and red dashed lines) is subtracted for better reading. In (b), the observational data from (Randel et al., 1999) are shown as grey-shaded area for comparison.

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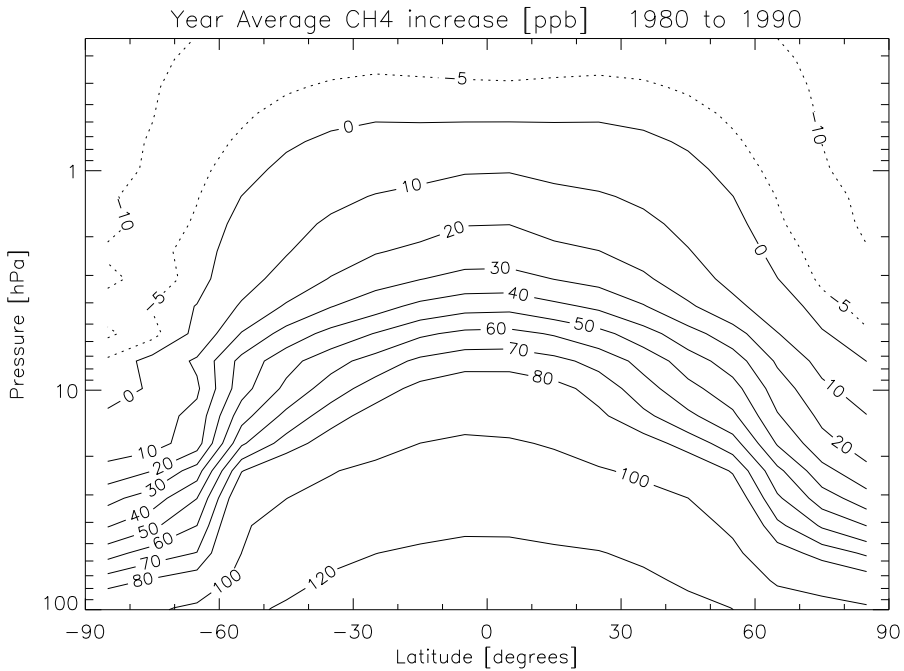

Fig. 2. Results from the Mainz photochemical 2-D model show the latitude dependence of the CH_4 trends in the stratosphere for the period 1980–1990.

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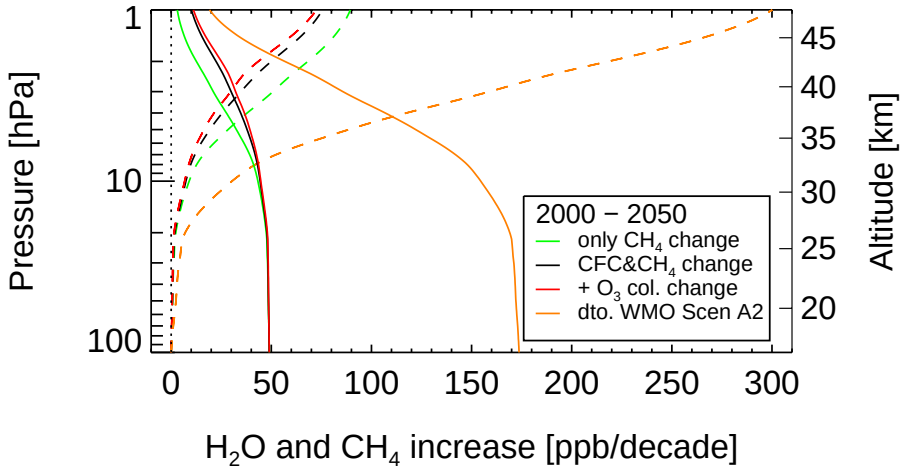

Fig. 3. Future scenario for the increase in stratospheric water vapor taking into account projections for CH_4 increase, the decrease in stratospheric chlorine and the recovery of stratospheric ozone. Solid lines show the CH_4 trends and dashed lines the H_2O trends. The green, black and red lines depict the individual effects calculated for a projected CH_4 increase according to the WMO baseline scenario (Table 12.2 in WMO, 1999). The orange line is the final result (i.e. corresponding to the red line) for a CH_4 increase according to WMO scenario A2 (Table 4B-3 in WMO, 2003).

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