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# Small Interannual Variability of Global Atmospheric Hydroxyl

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The oxidizing capacity of the global atmosphere is largely determined by hydroxyl (OH) radicals and is diagnosed by analyzing methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) measurements. Previously, large year-to-year changes in global mean OH concentrations have been inferred from such measurements, suggesting that the atmospheric oxidizing capacity is sensitive to perturbations by widespread air pollution and natural influences. We show how the interannual variability in OH has been more precisely estimated from  $\text{CH}_3\text{CCl}_3$  measurements since 1998, when atmospheric gradients of  $\text{CH}_3\text{CCl}_3$  had diminished as a result of the Montreal Protocol. We infer a small interannual OH variability as a result, indicating that global OH is generally well buffered against perturbations. This small variability is consistent with measurements of methane and other trace gases oxidized primarily by OH, as well as global photochemical model calculations.

The hydroxyl radical (OH) is the primary oxidant for many non- $\text{CO}_2$  greenhouse gases, several stratospheric ozone-depleting substances and their substitutes, and hazardous air pollutants. It is also central to atmospheric photochemistry and the regulation of tropospheric ozone, and thus controls the influence of chemically reduced trace gases on climate, the stratospheric ozone layer, and air quality (1–4). The interannual variability (IAV) in OH concentrations ([OH]) on large spatial scales provides insight into the stability of the atmospheric oxidation capacity and its sensitivity to human-induced and natural perturbations. However, a consistent, predictive understanding of the net response of [OH] on broad scales to such perturbations is lacking. For example, a range of negative [OH] feedbacks is calculated from changes in atmospheric methane abundance (3, 5–7).

Theory suggests that the sensitivity of [OH] to environmental changes depends on the relative importance of primary and secondary (recycling) OH formation pathways (7). The balance between primary OH formation initiated by ultraviolet light and formation by recycling is determined by atmospheric abundances and distributions of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{CO}$ , and  $\text{CH}_4$ , as well as other

parameters (3, 8), many of which are highly variable in space and time and are relatively poorly characterized on global scales and in model calculations. As a result, calculated sensitivities of global [OH] to IAV in the chemical and physical makeup of the atmosphere have yet to be adequately tested.

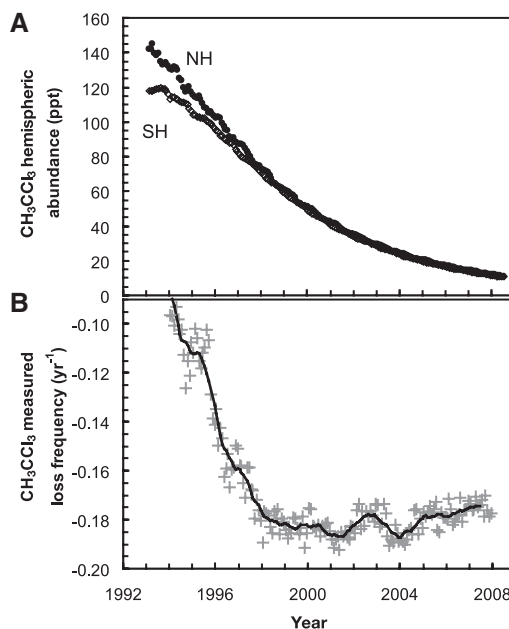
Although OH can be measured directly on local scales, these results cannot characterize the integrated response of global mean [OH] to the many processes that control its formation and loss. Instead, indirect techniques are used in which [OH] is derived from observations of OH-oxidized trace gases such as  $\text{CH}_3\text{CCl}_3$  and  $^{14}\text{CO}$  (9–19).

However, these approaches can suggest a very different sensitivity of [OH] to variations in the atmospheric environment than is derived in atmospheric models (20). Year-to-year changes in global [OH] as high as 20 to 25% have been derived from analyses of  $\text{CH}_3\text{CCl}_3$  observations between 1980 and 2003, and these analyses imply a mean IAV of 7 to 9% (16, 17). Chemistry transport models calculate a global [OH] variability of only 1 to 2%, but these models do not currently include variability in all factors influencing [OH] (20–23). Variations in [OH] of up to 20% have been estimated from  $^{14}\text{CO}$ , although only over a few months and on semihemispheric spatial scales (19).

Global mean [OH] can be estimated from atmospheric observations of a trace gas whose predominant sink is reaction with OH from mass balance considerations by equating the rate of change in the global burden ( $dG/dt$ ) to the difference between the global emission rate ( $E$ ) and loss. Solving for the pseudo-first-order rate constant for loss ( $k_G$ ), which is proportional to [OH], gives

$$[\text{OH}] \propto k_G = \frac{E}{G} - \frac{dG/dt}{G} \quad (1)$$

where  $G$  is the global burden estimated from surface measurements. Although  $\text{CH}_3\text{CCl}_3$  losses (and  $k_G$ ) are dominated by OH oxidation according to  $k(T) \times [\text{OH}]$ , they include stratospheric photolysis, hydrolysis in surface waters, and other processes. Global mean [OH] derived in this



**Fig. 1.** (A) Observed hemispheric monthly mean mixing ratios of  $\text{CH}_3\text{CCl}_3$  [update of (14)]. NH and SH denote Northern and Southern Hemispheres, respectively. (B) Exponential loss frequencies for  $\text{CH}_3\text{CCl}_3$  derived from global surface means. Gray points are independent estimates derived from monthly means 12 months apart [e.g.,  $\ln(G_{\text{Jan, 2007}}/G_{\text{Jan, 2006}})$ ] plotted at the midpoint of this interval; the black line is the 12-month running mean.

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way is implicitly weighted by the trace-gas loss frequency (or inverse lifetime,  $\tau^{-1}$ ). To account for non-OH losses that are assumed constant over interannual periods, anomalies in [OH] are augmented depending on the magnitude of OH oxidation relative to other losses (24).

We derived variability in [OH] during the period 1998–2007 from  $\text{CH}_3\text{CCl}_3$  observations made from paired-flask samples collected approximately weekly at nine remote sites across the globe (14, 24). We concentrate on this decade because it followed a rapid  $\text{CH}_3\text{CCl}_3$  emission decline owing to the revised and amended Montreal Protocol on Substances that Deplete the Ozone Layer. By 1998, yearly emissions of  $\text{CH}_3\text{CCl}_3$  had diminished to become only a small fraction of the amount of  $\text{CH}_3\text{CCl}_3$  annually removed by OH (fig. S1). Furthermore, uncertainties associated with estimating the global burden of  $\text{CH}_3\text{CCl}_3$  and its rate of change have also diminished (14). Under these conditions, the pseudo-first-order loss of  $\text{CH}_3\text{CCl}_3$ , and therefore global [OH], is more directly reflected in an observable quantity: the measured decline of  $\text{CH}_3\text{CCl}_3$  mixing ratios in the background atmosphere.

The rapid decline in  $\text{CH}_3\text{CCl}_3$  emissions during the mid-1990s led to a nearly constant exponential decay in global atmospheric  $\text{CH}_3\text{CCl}_3$  mixing ratios of  $-0.181 \pm 0.005 \text{ year}^{-1}$  during the period 1998–2007 (Fig. 1). From these observations, we derive a mean IAV in global [OH] of  $2.3 \pm 1.5\%$  during 1998–2007 (Fig. 2). Unlike the period before 1998, when the variability implied for [OH] depended strongly on the magnitude and uncertainty in emissions (16), the variability in [OH] derived since then is insensitive to the emissions chosen (24). This IAV is less than the mean variability calculated for OH since 1997 with  $\text{CH}_3\text{CCl}_3$  observations from an independent sampling network (25).

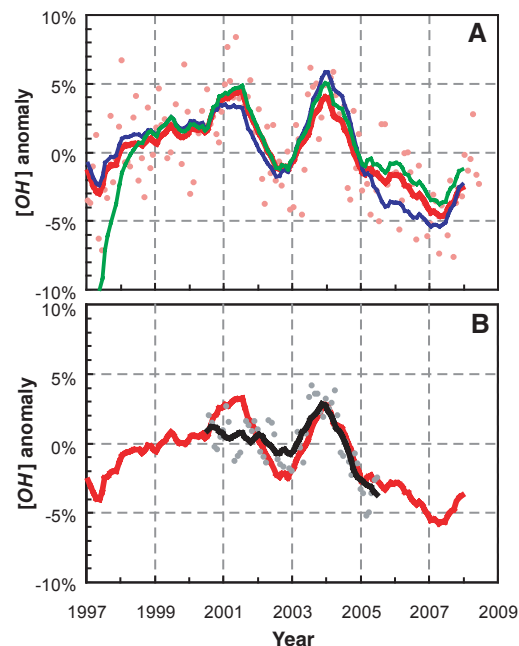
An IAV for [OH] of  $2.3 \pm 1.5\%$  during 1998–2007 is much smaller than the pre-1995 mean variability of  $\sim 7$  to 9% (up to 25%) derived previously (16, 17). We suggest that this difference arises because of reduced uncertainties in the analysis of  $\text{CH}_3\text{CCl}_3$  data during 1998–2007 rather than a substantial reduction in the variability of atmospheric oxidizing capacity after 1997. IAV in [OH] is more accurately determined since 1998 because uncertainties in both  $E/G$  and  $(dG/dt)/G$  have become smaller as  $\text{CH}_3\text{CCl}_3$  emissions declined rapidly in response to the Montreal Protocol phase-out of  $\text{CH}_3\text{CCl}_3$  production (14) (fig. S1). During the 1980s,  $E/G$  was 120% of  $k_G$ ; from 1990 to 1998,  $E/G$  was decreasing by 10 to 50% per year. For these periods, estimates of [OH] variability are highly sensitive to small errors in poorly constrained  $\text{CH}_3\text{CCl}_3$  emissions: We estimate that a small shift ( $\pm 0.25$  year) in the timing of emissions during 1990–1998 as production rapidly declined would cause a  $\pm 8\%$  change in the annual mean [OH] derived for these years. Since 1998, however,  $E/G$  has been a rather small and constant fraction ( $\sim 10\%$ ) of the derived  $k_G$  (fig. S1). Although emissions and their interannual changes

remain uncertain, their influence on estimates of  $k_G$  since 1998 has been substantially reduced.

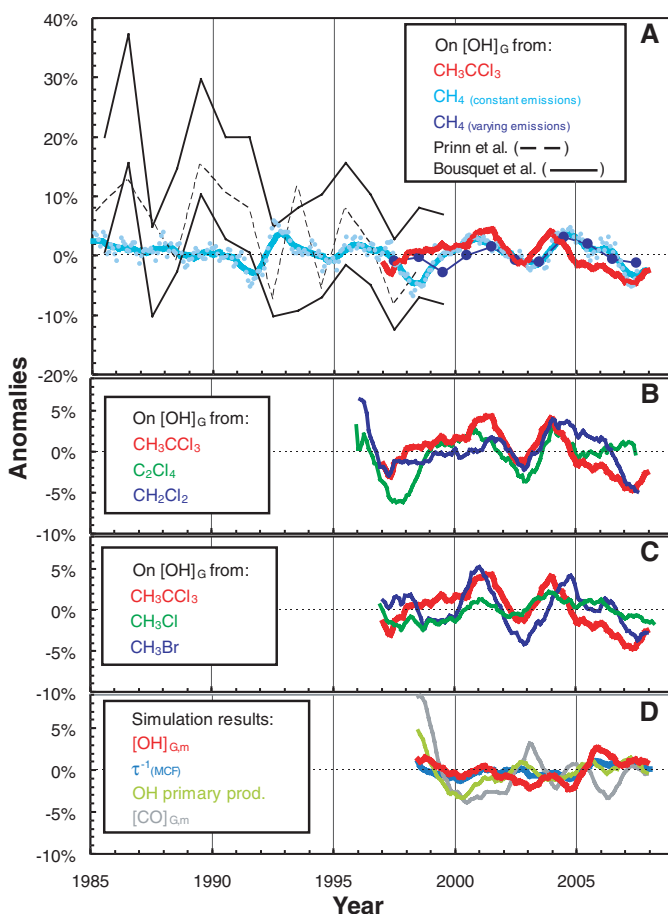
Uncertainty in  $(dG/dt)/G$  for  $\text{CH}_3\text{CCl}_3$  is also reduced since 1998 because its atmospheric gra-

dients have diminished substantially in response to near-zero emissions. Annual mean mixing ratio gradients between remote stations were as much as 30 to 40% of the global mean in the 1980s (17)

**Fig. 2.** Anomalies in global [OH] derived from NOAA  $\text{CH}_3\text{CCl}_3$  data with different modeling approaches and emissions. (A) [OH] anomalies inferred from measured global surface means of  $\text{CH}_3\text{CCl}_3$  and a box model (see text and Eq. 1) incorporating three different emission histories: emissions through 2000 (17) then declining exponentially thereafter at  $-20\% \text{ year}^{-1}$  (red line); those same emissions updated after 2002 with (25) (blue line); and zero emissions (green line). Anomalies are relative to mean [OH] during 1998–2007. Points represent an [OH] anomaly derived from two monthly means 12 months apart and exponentially declining emissions after 2000 (see above); smoothed lines are 12-month running means. (B) [OH] anomalies derived from a high-resolution 3D inversion of the NOAA flask data (points and black line) (18) and exponentially declining emissions. Modeled anomalies determined for yearly intervals centered about each month during 2000–2005 (gray points) are smoothed over 12-month periods (black line) to allow a consistent comparison with box model results. The red line is repeated from the top panel but is calculated relative to mean [OH] during 2000–2005 to be consistent with the modeled period.



**Fig. 3.** Anomalies in [OH] inferred from trace gas data and calculated in a global model simulation. (A) Anomalies inferred from NOAA  $\text{CH}_3\text{CCl}_3$  data [red line from Fig. 2; also in (B) and (C)]; from global  $\text{CH}_4$  data with constant or varying emissions; from Bousquet *et al.* (16) (range includes internal and external uncertainties); and from Prinn *et al.* (17). Anomalies are relative to estimates after 1997. (B and C) [OH] anomalies inferred from NOAA measurements of multiple trace gases [see text and (24)]. (D) Model simulated [OH] anomalies weighted by mass ( $[\text{OH}]_{G,m}$ ) or expressed as the  $\text{CH}_3\text{CCl}_3$  loss frequency ( $\tau^{-1}_{(MCF)}$ ). Simulated anomalies in OH primary production ( $\text{O}^1\text{D} + \text{H}_2\text{O}$ ) and CO weighted by mass ( $[\text{CO}]_{G,m}$ ) are also shown (24, 30).



compared to ~7% since 1998 (14). Diminished gradients result in improved estimates of [OH] variability because of reduced errors in estimating the global  $\text{CH}_3\text{CCl}_3$  burden ( $G$ ) and its rate of change ( $dG/dt$ ) from measurements at a small number of sampling sites (fig. S2).

Our box model approach and previous calculations (17) have shortcomings that could affect conclusions regarding [OH] in the presence of large  $\text{CH}_3\text{CCl}_3$  emissions (26). To investigate these influences during a period when  $\text{CH}_3\text{CCl}_3$  emissions and atmospheric mixing ratio gradients are reduced and transport-related errors are therefore minimized, we derived [OH] variability with a three-dimensional inversion technique that includes interannually varying meteorology (18). In this approach, the monthly global [OH] during 2000–2005 is optimized by minimizing the differences between modeled and observed  $\text{CH}_3\text{CCl}_3$  (24). Results for 2000 to 2005 are highly consistent with the box model analysis and suggest an annual mean [OH] IAV of  $2.3 \pm 1.2\%$  (Fig. 2B). Thus, in the absence of substantial  $\text{CH}_3\text{CCl}_3$  emissions, a similar year-to-year variability magnitude in mean [OH] is calculated with different methods from measurements of  $\text{CH}_3\text{CCl}_3$ .

A reliable estimate of [OH] variability must be consistent with observations of other trace gases oxidized by OH. We derived estimates of [OH] variability by applying Eq. 1 to global  $\text{CH}_4$  observations from an independent sampling network (24, 27). A mean IAV for [OH] of  $2.1 \pm 1.8\%$  is implied during 1985–2008, assuming constant  $\text{CH}_4$  emissions (Fig. 3A). This estimate is likely an upper limit, however, because methane emissions vary on interannual time scales. When interannual changes in  $\text{CH}_4$  emissions from biomass burning and wetlands during 1998–2007 are included (24, 28, 29), an IAV for [OH] of  $1.8 \pm 1.2\%$  is inferred for this period, which is less than the variability in [OH] of  $2.9 \pm 1.9\%$  derived for 1998–2007 assuming constant methane emissions (Fig. 3A).

Our analysis of methane allows three important conclusions. First, when emissions variations of methane are considered, implied global [OH] variability is reduced. This is consistent with the anticorrelation expected between methane and [OH], all other things being constant (3). It is unlikely that global annual  $\text{CH}_4$  emissions varied coherently with [OH] during the 1980s and 1990s by up to the 25% needed to mask large OH changes implied from  $\text{CH}_3\text{CCl}_3$  analyses for these years. Second, the IAV in global [OH] implied from methane has been quite constant at about 2% over 25 years, a period during which global anthropogenic emissions of gases that affect OH varied substantially. Hence, a substantial reduction in [OH] variability as inferred from an analysis of  $\text{CH}_3\text{CCl}_3$  observations before and after 1997 seems unlikely. Third, the global [OH] variability implied from methane is consistent with that implied from  $\text{CH}_3\text{CCl}_3$  only after 1997. This confirms that the reduced uncertainties associated with estimating [OH] variability from  $\text{CH}_3\text{CCl}_3$

after 1997 allow a more accurate diagnosis of global [OH] variations during this period.

We applied this same methodology to observations of additional gases oxidized primarily by OH ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{CH}_2\text{Cl}_2$ ). Although interannual variations in emissions of these chemicals are poorly characterized, they arise from a variety of natural and anthropogenic processes. As a result, consistent variability in atmospheric abundances of these compounds implies changes in oxidation by the OH radical. By accounting for multiyear changes in trace-gas emissions with smoothed fits to observed global mixing ratios and, for the methyl halides, annual variations in biomass burning and industrial emission (table S1 and figs. S3 and S4), we derived variations in annual [OH] needed to account for the trace-gas residual mixing ratio variations. The results for these four gases imply IAV in global [OH] of 1 to 3% since the late 1990s (Fig. 3, B and C), consistent with the small [OH] variability derived from  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_4$ .

These results also suggest that the timings of [OH] variations derived with these four additional trace gases are similar to those derived from methane and  $\text{CH}_3\text{CCl}_3$  (Fig. 3, A to C). [OH] values derived for 1997–1999, 2002–2003, and 2006–2007 are consistently lower than those derived during 2000–2001 and 2004–2005 for all of the trace gases considered. Less consistency is derived for 1997–1998, but during this period variations implied from  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CH}_3\text{Br}$  depend strongly on uncertain emission magnitudes from enhanced biomass burning, likely associated with the strong El Niño then (Fig. 3, A and C, and fig. S4).

A theory-based estimate of [OH] variability was also derived with an atmospheric chemistry general circulation model for 1998 to June 2008 in which assimilated observed meteorology was used (24, 30). In this model, [OH] is calculated from a suite of chemical and physical parameters that vary over time and space with consideration of IAV in water vapor, photolysis rates, and biomass burning (Fig. 3D and figs. S5 and S6). Although the detailed variations implied from our trace-gas observations are not well reproduced in the model simulation, a low IAV in global tropospheric [OH] of  $0.9 \pm 0.8\%$  is calculated (weighted by mass or the  $\text{CH}_3\text{CCl}_3$  loss frequency), consistent with the [OH] variations derived from the trace-gas data, which are likely to be upper limits (24). This small [OH] variability is derived even though simulated variabilities for primary OH production and mixing ratios of  $\text{CO}$ , a strong sink for tropospheric OH (3), are calculated to be substantially larger. A small variability (<2%) was also suggested for annual mean [OH] from independent model simulations of the period 1979–2001 (21–23).

These observationally derived results substantially clarify our understanding of the sensitivity of Earth's atmospheric oxidizing capacity to environmental perturbations. Both observations and model calculations demonstrate that global mean

[OH] is well buffered on interannual time scales, consistent with both primary and secondary OH formation pathways and atmospheric oxidant transport playing important roles in maintaining its global abundance. The improved understanding of this fundamental atmospheric property thus enables more reliable projections of trace-gas climate forcing and atmospheric oxidizing capacity given expected changes in future anthropogenic emissions.

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## Supporting Online Material

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