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 (CH$_3$CCl$_3$) measurements. Previously, large year-to-year changes in 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 CH$_3$CCl$_3$ measurements since 1998, when atmospheric gradients of CH$_3$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.

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 CH$_3$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 $^{14}$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

$$[\text{OH}] \propto \frac{E}{G} - \frac{dG}{dt} \frac{G}{G}$$

where $G$ is the global burden estimated from surface measurements. Although CH$_3$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 way is insensitive to changes in [OH].

Fig. 1. (A) Observed hemispheric monthly mean mixing ratios of CH$_3$CCl$_3$ [update of (14)]. NH and SH denote Northern and Southern Hemispheres, respectively. (B) Exponential loss frequencies for CH$_3$CCl$_3$ derived from global surface means. Gray points are independent estimates derived from monthly means 12 months apart [e.g., $\ln(G_{Jan.2007}/G_{Jan.2006})$] plotted at the midpoint of this interval; the black line is the 12-month running mean.
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 CH$_3$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 CH$_3$CCl$_3$ emission decline owing to the revised and amended Montreal Protocol on Substances that Deplete the Ozone Layer. By 1998, yearly emissions of CH$_3$CCl$_3$ had diminished to become only a small fraction of the amount of CH$_3$CCl$_3$ annually removed by OH (fig. S1). Furthermore, uncertainties associated with estimating the global burden of CH$_3$CCl$_3$ and its rate of change have also diminished (14).

Under these conditions, the pseudo-first-order loss of CH$_3$CCl$_3$, and therefore global [OH], is more directly reflected in an observable quantity: the measured decline of CH$_3$CCl$_3$ mixing ratios in the background atmosphere.

The rapid decline in CH$_3$CCl$_3$ emissions during the mid-1990s led to a nearly constant exponential decay in global atmospheric CH$_3$CCl$_3$ mixing ratios of $-0.181 \pm 0.005$ year$^{-1}$ during the period 1998–2007 (Fig. 1). From these observations, we derive an 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 CH$_3$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 CH$_3$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 CH$_3$CCl$_3$ emissions declined rapidly in response to the Montreal Protocol phase-out of CH$_3$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 CH$_3$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 CH$_3$CCl$_3$ is also reduced since 1998 because its atmospheric gradients 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). We derived variability in [OH] during the period 1998–2007 from CH$_3$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 CH$_3$CCl$_3$ emission decline owing to the revised and amended Montreal Protocol on Substances that Deplete the Ozone Layer. By 1998, yearly emissions of CH$_3$CCl$_3$ had diminished to become only a small fraction of the amount of CH$_3$CCl$_3$ annually removed by OH (fig. S1). Furthermore, uncertainties associated with estimating the global burden of CH$_3$CCl$_3$ and its rate of change have also diminished (14).

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compared to ~7% since 1998 (14). Diminished gradients result in improved estimates of [OH] variability because of reduced errors in estimating the global CH$_4$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] variability because of 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 CH$_4$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 ± 1.2% (Fig. 2B). Thus, in the absence of substantial CH$_3$CCl$_3$ emissions, a similar year-to-year variability magnitude in mean [OH] is calculated with different methods from measurements of CH$_3$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 CH$_4$ observations from an independent sampling network (24, 27). A mean IAV for [OH] of 2.1 ± 1.8% is implied during 1985–2008, assuming constant 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 CH$_4$ emissions from biomass burning and wetlands during 1998–2007 are included (24, 28, 29), an IAV for [OH] of 1.8 ± 1.2% is inferred for this period, which is less than the variability in [OH] of 2.9 ± 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 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 CH$_3$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 CH$_3$CCl$_3$ observations before and after 1997 seems unlikely. Third, the global [OH] variability implied from methane is consistent with that implied from CH$_3$CCl$_3$ only after 1997. This confirms that the reduced uncertainties associated with estimating [OH] variability from CH$_3$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 (CH$_3$Cl, CH$_3$Br, C$_2$Cl$_6$, and CH$_3$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 multyear 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 CH$_3$CCl$_3$ and 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 CH$_3$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 CH$_3$Cl, CH$_3$Br and CH$_4$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 (26). 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 ± 0.8% is calculated (weighted by mass or the CH$_3$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 CO, a strong sink for tropospheric OH (3), 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).

References and Notes
24. See supporting material on Science Online.

Supporting Online Material
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Materials and Methods
OMT Text
Figs. S1 to S6
Table S1
References
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