Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.
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Supplementary Information for

Hydrogen peroxide emissions from surface cleaning in a single-family residence

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SUPPLEMENTAL METHODS

Determination of peaks for kinetic analysis

Decay rate constants of H_2O_2 (k) were calculated using first-order exponential regression (Eq. 1) for selected H_2O_2 emission profiles following cleaning events. For such analysis, we either removed the large fluctuations (i.e., sharp spikes) seen in most of the cleaning events (as illustrated in Figure S2) or selected an adequate C_o (the initial mixing ratio) to minimize the large fluctuations.

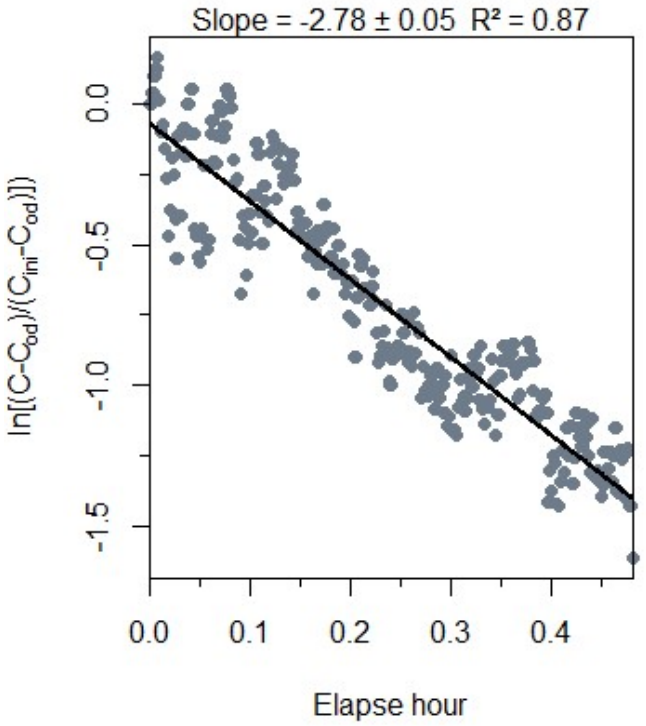

Figure S1. *Representative log-normalized decay profile for near counter experiment during regular cleaning. Slope represents the decay rate constant (k).*

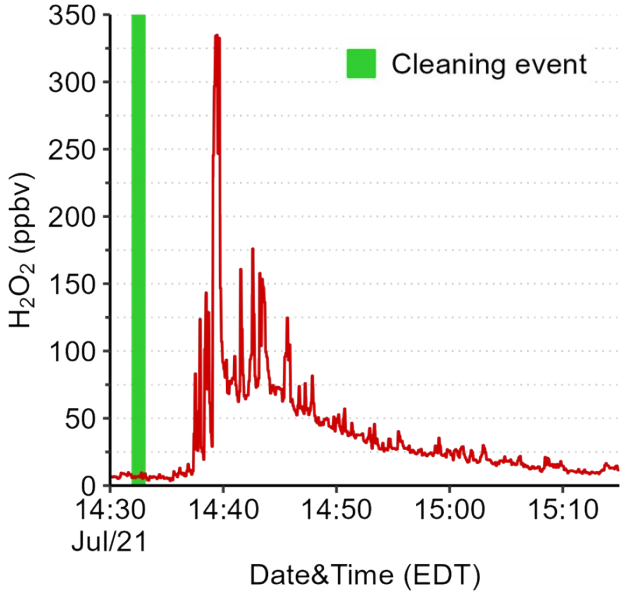

Figure S2. *Temporal profile of H_2O_2 mixing ratios observed in the house for a regular cleaning of dining room table when doors/windows were closed.*

OH steady-state concentration ($[OH]_{ss}$)

Predicted $[OH]_{ss}$ was calculated using the simplified steady-state approximation described by Zhou et al.:[1]

$$[OH]_{SS} = \frac{J_{HONO}[HONO] + 2J_{H_2O_2}[H_2O_2]}{k_{OH+NO}[NO] + k_{OH+NO_2}[NO_2] + k_{OH+HONO}[HONO]} \quad [S1]$$

where J_{HONO} and $J_{H_2O_2}$ are the photolysis rate constants (s^{-1}) of nitrous acid and hydrogen peroxide, respectively; k_{OH+NO}, k_{OH+NO_2}, $k_{OH+HONO}$, and $k_{OH+H_2O_2}$ are the rate constants (cm^3 $molec^{-1}$ s^{-1}) for the reactions between OH and NO, OH and NO_2, OH and HONO, and OH and H_2O_2, respectively; and $[X]$ represents the concentration of gas-phase species (molecule cm^{-3}), with X = HONO, H_2O_2, NO, or NO_2.

Hydrogen peroxide can be a sink for OH (R1). We do not expect reaction with H_2O_2 to contribute greatly to OH loss, as HO_2 reacts quickly with NO to form OH (R2). Nitric oxide concentrations in residences are on the order of 1×10^{11} molecule cm^{-3} (4 ppbv) in the absence of combustion (e.g., use of gas stoves).[2] At these NO concentrations we can assume that HO_2 is rapidly converted to OH, and loss of OH to reaction with H_2O_2 can be rejected. This assumption is also made for loss of OH to reaction with volatile organic compounds (VOCs), which also results in the formation of HO_2. However, we also calculated $[OH]_{ss}$ with loss to reaction with H_2O_2 included to provide a lower limit for $[OH]_{ss}$ (S2).

$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad \text{[R1]}$$

$$\quad \text{[R2]}$$

$$[OH]_{SS} = \frac{J_{HONO}[HONO] + 2J_{H_2O_2}[H_2O_2]}{k_{OH+NO}[NO] + k_{OH+NO_2}[NO_2] + k_{OH+HONO}[HONO] + k_{OH+H_2O_2}[H_2O_2]} \quad \text{[S2]}$$

Table S3 shows kinetic parameters used for $[OH]_{ss}$ calculations. Table S4 shows predicted $[OH]_{ss}$ with and without H_2O_2 included as a sink at the H_2O_2 concentrations shown in Table 3. When loss to H_2O_2 was not considered, $[OH]_{ss}$ was predicted to increase by up to 21% compared to pre-cleaning levels (i.e., with HONO photolysis as the sole OH source), but including it led to a predicted reduction in $[OH]_{ss}$ of 91%.

Table S1. *Values used for determining $[OH]_{ss}$ in Eq. S1. Photolysis rate constants (J) are from Kowal et al.[3], and the rate constants (k_{OH+X}) are from Burkholder et al.[4]*

Gas-phase species	J (s^{-1})	k_{OH+X} (cm^3 $molec^{-1}$ s^{-1})	[X] (molec cm^{-3})
H_2O_2	1.4×10^{-7}	1.8×10^{-12}	Varies[a]
HONO	2.2×10^{-4}	6.9×10^{-12}	1.2×10^{11}
NO	-	7.4×10^{-12}	1.0×10^{11}
NO_2	-	1.3×10^{-11}	1.0×10^{11}

a) Presented on Table 3 and Table S4 with units of ppbv

Table S2. *Predicted $[OH]_{ss}$ following cleaning in sunlit air volumes using steady-state calculations Eq. S1 (H_2O_2 not considered a sink) and S2 (H_2O_2 considered a sink).*

$[H_2O_2]$ (ppb)	$[OH]_{ss}$ from Eq. S1 (10^6 molecule cm^{-3})	$[OH]_{ss}$ from Eq. S2 (10^6 molecule cm^{-3})
1	9.4	9.3
135	9.7	3.1
323	10.2	1.7
840	11.4	0.8

While ignoring H_2O_2 as an OH sink may be overly simplistic, the small increases in $[OH]_{ss}$ using this approach (i.e., Eq. S1) are in good agreement with those from Zhou et al.[5] In that work, $[OH]_{ss}$ was predicted using an indoor atmospheric chemistry box model.[5] The model used was based on the master chemical model (MCM) and included explicit chemical reactions for ~5000 distinct species. Loss of OH to reaction with H_2O_2 and VOCs was included in the steady-state calculations, as was regeneration of OH from HO_2 via R2.[6] In that work, the model predicted peak $[OH]_{ss}$ to increase by ~10% when measured H_2O_2 concentrations increased to ~313 ppbv following cleaning.[5] Using Eq. S1, we predict $[OH]_{ss}$ to increase by ~8% at that H_2O_2 concentration. Conversely, using Eq. S2 results in a predicted *decrease* of $[OH]_{ss}$ of ~81%. The agreement with $[OH]_{ss}$ predicted by the box model obtained by Eq. S1 gives us confidence that this simplified steady-state equation is appropriate for $[OH]_{ss}$ calculation under the conditions of this study, and that R1 should not be included as a loss term for OH. We note that this approach is valid when NO levels are high. When NO levels are low (due, for example, to titration by O_3), HO_2 will not be completely converted to OH, and R1 might become a permanent sink. For example, we used the box model described above to calculate radical concentrations in a hospital room during the use of common gas-phase disinfectants including H_2O_2.[7] At high H_2O_2 concentrations (up to 500 ppmv is used during disinfection), $[OH]_{ss}$ was predicted to be only ~30% of that in the absence of added H_2O_2, despite very large OH formation rates (on the order of 109 molecule cm^{-3} s^{-1}). This decrease was attributed to OH loss via R1. Once H_2O_2 levels in the room decayed to 1 ppmv, we predicted $[OH]_{ss}$ to have increased to 70% of initial levels. We note that predicted NO concentrations in the hospital room were <150 pptv; regeneration of OH from HO_2 via R2 will be much slower than in residences, where NO concentrations are often more than 20× higher.

ADDITIONAL SUPPLEMENTAL FIGURES

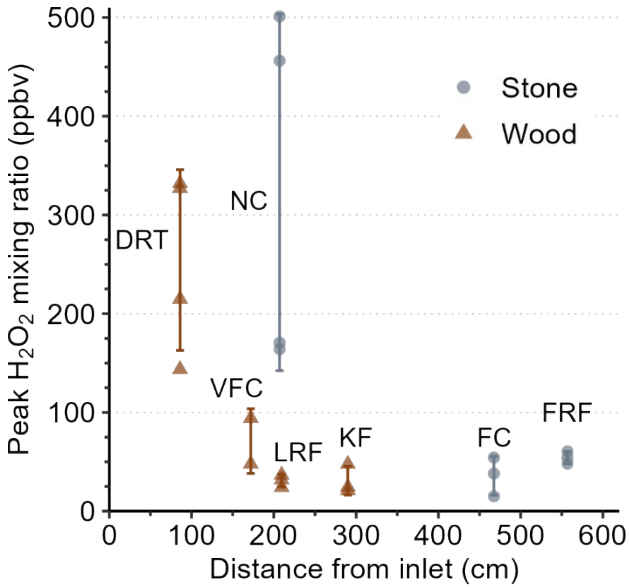

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Figure S3. *Peak H_2O_2 levels as a function of average distance from inlet for controlled regular cleaning events. Abbreviated texts indicate surface types listed in Table 1. Error bars represent the standard deviation.*

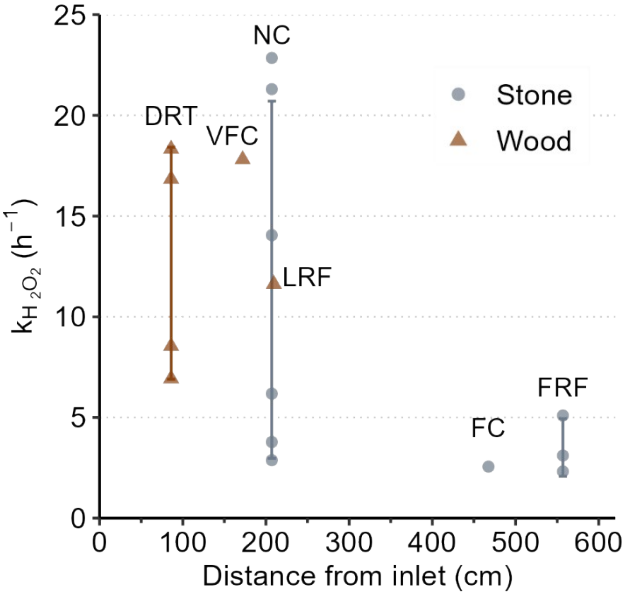

Figure S4*. H_2O_2 decay rate constants as a function of average distance from inlet for controlled regular cleaning events. Abbreviated texts indicate surface types listed in Table 1. Error bars represent the standard deviation.*

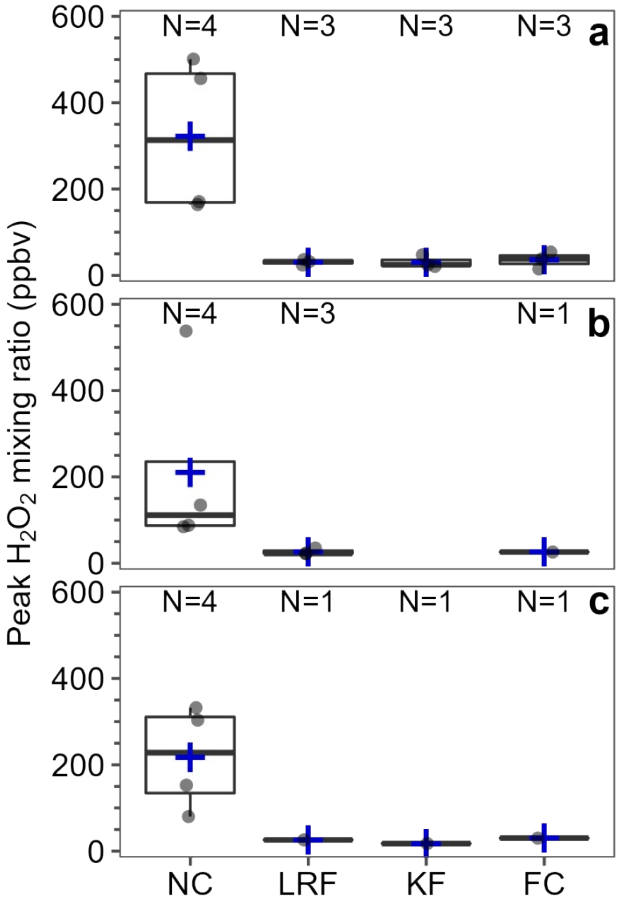

Figure S5. *Statistics of peak H_2O_2 levels for regular cleaning of four surfaces under different conditions:* ***(a)*** *full area cleaned with closed doors/windows,* ***(b)*** *half area cleaned with closed doors/windows, and* ***(c)*** *full area cleaned with patio doors open. The box and whisker plots show the median (line), mean (blue marker), first and third quartiles (box), and minima and maxima (whiskers). The number over each box and whisker plot indicates the number of cleaning events for that condition.*

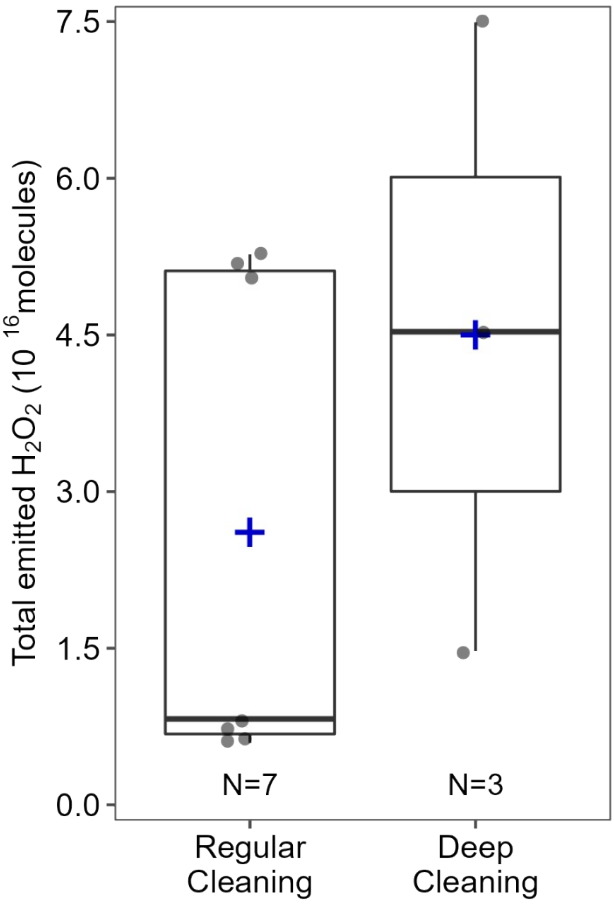

Figure S6. *Statistics of total emitted H_2O_2 molecules for regular and deep cleaning of the near counter and living room floor. The box and whisker plots show the median (line), mean (blue marker), first and third quartiles (box), and minimum and maximum (whiskers). The number under each box and whisker plot indicates the number of cleaning events for that condition.*

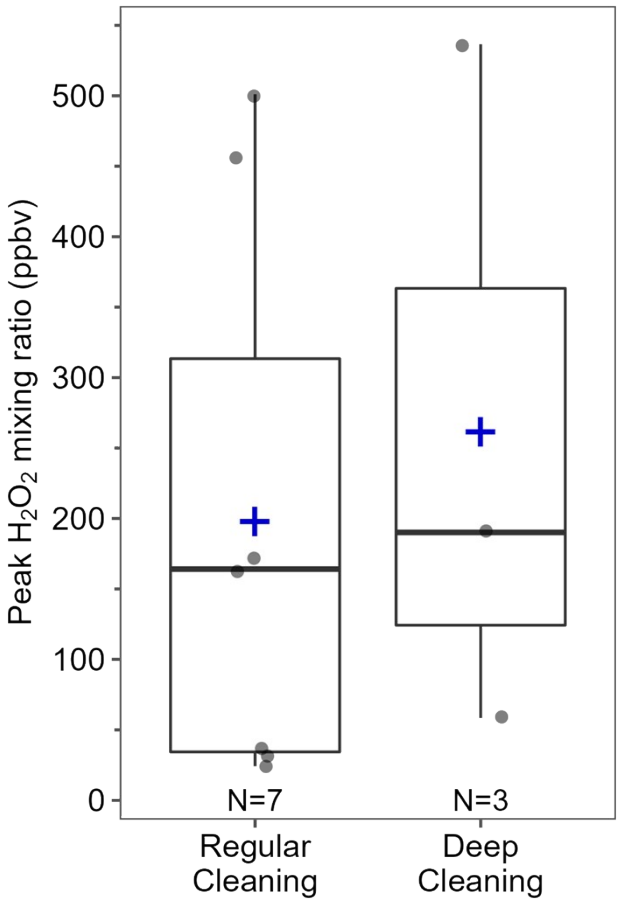

Figure S7*. Statistics of peak H_2O_2 levels for regular and deep cleaning of the near counter and living room floor. The box and whisker plots show the median (line), mean (blue marker), first and third quartiles (box), and minimum and maximum (whiskers). The number under each box and whisker plot indicates the number of cleaning events for that condition.*

ADDITIONAL SUPPLEMENTAL TABLES

Table S3. *Mean peak and total H_2O_2 mixing ratios and mean decay rate constants (k_{H2O2}) for cleaning events when full and half area were cleaned.*

Surface	Full area cleaned				Half area cleaned			
	Peak H_2O_2 (ppbv)	**Total H_2O_2 (10^{15} molecules)**	**k_{H2O2} (h^{-1})**	**N**	**Peak H_2O_2 (ppbv)**	**Total H_2O_2 (10^{15} molecules)**	**k_{H2O2} (h^{-1})**	**N**
NC	323 ± 181	40.5 ± 22.3	11.8 ± 8.9	4	211 ± 219	21.5 ± 17.1	14.7 ± 8.3	4
LRF	31.0 ± 6.4	6.86 ± 1.21	11.6	3	27.0 ± 7.5	4.53 ± 1.39	-	3
KF	31.0 ± 14.5	8.86 ± 4.40	-	3	-	-	-	0
FC	35.8 ± 19.7	10.8 ± 8.4	2.56	3	26.2	7.58	-	1

Table S4. *Mean peak mixing ratios, total H_2O_2 molecules emitted, and mean decay rate constants (k_{H2O2}) for cleaning events when doors/windows were closed and opened.*

Surface	Closed doors/windows				Opened doors/windows			
	Peak H_2O_2 (ppbv)	**Total H_2O_2 ($\times 10^{15}$ molecules)**	**k_{H2O2} (h^{-1})**	**N**	**Peak H_2O_2 (ppbv)**	**Total H_2O_2 ($\times 10^{15}$ molecules)**	**k_{H2O2} (h^{-1})**	**N**
NC	323 ± 181	40.5 ± 22.3	11.8 ± 8.9	4	217 ± 121	31.8 ± 14.6	27.4 ± 22.8	4
LRF	31.0 ± 6.4	6.86 ± 1.21	11.6	3	26.2	4.05	-	1
KF	31.0 ± 14.5	8.86 ± 4.40	-	3	17.8	6.76	-	1
FC	35.8 ± 19.7	10.8 ± 8.4	2.56	3	30.3	6.56	4.9	1

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