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How consistent are top-down hydrocarbon emissions based on formaldehyde observations from GOME-2 and OMI?

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Abstract. This supplement provides a description of the oxidation mechanism of OAHC (other anthropogenic hydrocarbons) in the IMAGESv2 CTM. The mechanism is adjusted in order to reproduce the yields of HCHO from the mix of 32 higher NMVOCs. The adjustment is based on box model calculations using the semi-explicit Master Chemical Mechanism (MCMv3.2).

1 HCHO from anthropogenic NMVOC emissions

Based on the NMVOC speciation profile of the UK National Atmospheric Emissions Inventory (NAEI) (Goodwin et al., 2001), 49 out of the 650 considered compounds account for ca. 81% of the total UK emission. 17 of the 49 compounds are included explicitly in IMAGESv2, namely, ethane, propane, ethene, propene, acetylene, formaldehyde, acetaldehyde, propanal, benzene, toluene, xylenes, methanol, ethanol, formic acid, acetic acid, acetone, and methyl ethyl ketone. The remaining 32 species (Table S1) are taken into account through a lumped compound, OAHC (other anthropogenic hydrocarbons). The oxidation mechanism of OAHC is adjusted in order to reproduce the yields of HCHO from the mix of 32 higher NMVOCs. This adjustment is realized based on time-dependent box model calculations using the semi-explicit Master Chemical Mechanism (MCMv3.2, http://mcm.leeds.ac.uk/MCM/, Saunders et al. (2003); Bloss et al. (2005)).

The simulations start at 6 a.m. for a temperature of 300 K at a mid-latitude location (30°N) in June. The initial concentrations of O_3, CO, and OAHC are set at 35 ppb, 200 ppb and 1 ppb, respectively. The NO_2 concentration is kept equal to 1 ppb since our focus is on environments dominated by anthropogenic activities. For each NMVOC, the HCHO yield is calculated after one day of simulation (short-term) and after 60 days (final). The short-term yield is defined as $Y_{1\mathrm{d}} = P_{1\mathrm{d}}/C_0$, where C_0 is the initial OAHC concentration and $P_{1\mathrm{d}}$ is the HCHO produced after one day. The final yield is calculated as $Y_{60\mathrm{d}} = P_{60\mathrm{d}}/\Delta C$, ΔC being the difference between the initial and the final OAHC concentration. Whereas the final yield is most relevant for estimating the impact of a precursor VOC on the global HCHO budget, the short-term yield best reflects the impact of this compound in the vicinity of its emission region.

The calculated short-term and final molar yields are summarized in Table S1. As expected, the highest short-term yields are calculated for the most reactive precursors, namely, the higher alkenes and aromatics, with k_{OH} typically ranging between $3{\cdot}10^{-11}$ and $7{\cdot}10^{-11}$ cm^3 molec.$^{-1}$ s^{-1}. For those compounds, the short-term yield and the final yield are very close, within $\sim$ 10%. Exceptions are the cases of ethylbenzene, which is less reactive, and 2-methylpropene, which is oxidized to acetone, a very slow-reacting intermediate. For alkanes, alcohols and esters, the short-term yield is often much lower than the final yield, due to the relatively low reactivity of the precursor (k_{OH} between $2{\cdot}10^{-12}$ and $13{\cdot}10^{-12}$ cm^3 molec.$^{-1}$ s^{-1}) and/or due to the existence of slow-reacting oxygenated intermediates.

For alkanes, the highest final yields are calculated for branched-chain structures (0.5-0.66 per carbon). The yields are slightly lower for butane and pentane (0.5 per C) and significantly lower for the longer linear alkanes (<0.4 per C). Final yields range between 0.43 and 0.72 per C for alkenes, and between 0.33 and 0.35 for trimethylbenzenes.

The production of HCHO (in g) by a NMVOC can be expressed as

$$P = E \cdot Y \cdot \mathrm{MW}_{\mathrm{HCHO}}/\mathrm{MW}_{\mathrm{NMVOC}}, \quad (1)$$

with E the emission (in g), Y the calculated short-term or final molar yield and MW the molecular weight.

The emission of the lumped OAHC species being taken equal to the total emission (in g) of the explicit NMVOCs, its molecular weight is calculated using

$$\mathrm{MW}_{\mathrm{OAHC}} = \frac{\sum_i E_i}{\sum_i (E_i/\mathrm{MW}_i)}, \quad (2)$$

and its short-term and final yield by

$$Y_{\mathrm{OAHC}} = \frac{\sum_i (E_i/\mathrm{MW}_i) \cdot Y_i}{\sum_i E_i/\mathrm{MW}_i}. \quad (3)$$

The values obtained in this way are 73 g(HCHO)/g(OAHC) for $\mathrm{MW}_{\mathrm{OAHC}}$ and 0.567 and 2.381 for the short-term and final yields, respectively.

The rate of the reaction of OAHC with OH,

$$\mathrm{OAHC} + \mathrm{OH} \rightarrow \mathrm{KO2} \quad (4)$$

needed to reproduce those yields is relatively low ($1.7{\cdot}\,10^{-12}$ cm^3 molec.$^{-1}$ s^{-1}) based on box model calculations. The following simple mechanism is adopted :

$$\mathrm{KO2} + \mathrm{NO} \rightarrow 0.1\,\mathrm{KONO2} + 0.9\,(\mathrm{KO} + \mathrm{NO_2}) \quad (5)$$

$$\mathrm{KO2} + \mathrm{HO_2} \rightarrow \mathrm{KOOH} \quad (6)$$

$$\mathrm{KO2} + \mathrm{CH_3O_2} \rightarrow 0.6\,(\mathrm{KO} + \mathrm{CH_3O}) + 0.2\,(\mathrm{KOH} + \mathrm{HCHO}) + 0.2\,(\mathrm{MEK} + \mathrm{CH_3OH}), \quad (7)$$

where MEK denotes methylethyl ketone, KOH is a generic higher alcohol and the oxy radical (KO) reacts immediately

following

$$\begin{aligned}\mathrm{KO} \rightarrow\ & 0.14\,\mathrm{CH_3COCH_2O_2} + 0.14\,\mathrm{HO_2} \\ & + 0.32\,\mathrm{HOCH_2CH_2O_2} + 0.46\,\mathrm{CH_3CHO} \\ & + 0.46\,\mathrm{CH_3CO_3} + 0.08\,\mathrm{CH_3COCH_3}.\end{aligned}$$

Both KONO2 and KOOH photolyze (to KO + NO_2 and KO + OH, respectively) and react with OH :

$$\mathrm{KONO2} + \mathrm{OH} \rightarrow \mathrm{NO_2} + \mathrm{CH_3CHO} + \mathrm{CH_3CO_3} \qquad (8)$$

$$\begin{aligned}\mathrm{KOOH} + \mathrm{OH} \rightarrow\ & 0.4\,(\mathrm{BIACET} + \mathrm{OH} + \\ & \mathrm{CH_3COCH_2O_2}) + 0.1\,\mathrm{KO2},\end{aligned} \qquad (9)$$

where BIACET denotes biacetyl ($CH_3COCOCH_3$). The kinetic rates are k_5 = 2.54·10^{-12} exp(360/T), k_6 = 1.82·10^{-13} exp(1300/T), k_7 = 3.8·10^{-13}, k_8 = 10^{-12}, and k_9 = 3.9·10^{-11} (in cm^3 molec.$^{-1}$ s^{-1}), where T denotes the temperature.

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Table S1. MCMv3.2-based short-term yields (after 1 day) and final yields (after 60 days) of HCHO from the oxidation of NMVOCs not explicitly considered in the IMAGES mechanism. The OH-reaction rates at 298 K and the estimated emissions for the UK (Goodwin et al., 2001) are also provided.

	NMVOC	Molecular weight	$Y_{1\mathrm{d}}$ mol/mol	$Y_{60\mathrm{d}}$ mol/mol	OH-reaction rate $\mathrm{cm^3 molec.^{-1} s^{-1}}$	Emission kt/yr
Higher alkanes	butane	58	0.280	2.033	$2.35 \cdot 10^{-12}$	151.11
	pentane	72	0.600	2.098	$4.00 \cdot 10^{-12}$	64.53
	hexane	86	0.624	2.805	$5.45 \cdot 10^{-12}$	51.46
	heptane	100	0.520	2.952	$7.02 \cdot 10^{-12}$	22.49
	octane	114	0.505	2.976	$8.70 \cdot 10^{-12}$	15.08
	nonane	128	0.541	3.128	$9.98 \cdot 10^{-12}$	6.03
	decane	142	0.607	3.826	$1.12 \cdot 10^{-11}$	11.04
	undecane	156	0.717	4.339	$1.29 \cdot 10^{-11}$	4.87
	2-methylpropane	58	0.308	2.710	$2.18 \cdot 10^{-12}$	40.92
	2-methylbutane	72	0.361	2.810	$3.70 \cdot 10^{-12}$	70.18
	2-methylpentane	86	0.530	2.914	$5.30 \cdot 10^{-12}$	5.73
	3-methylpentane	86	0.683	2.994	$5.40 \cdot 10^{-12}$	3.96
	2-methylhexane	100	0.525	3.814	$6.86 \cdot 10^{-12}$	5.36
	3-methylhexane	100	0.670	3.283	$7.15 \cdot 10^{-12}$	4.38
	cyclohexane	86	0.541	1.615	$7.20 \cdot 10^{-12}$	4.31
Higher alkenes	1-butene	56	1.790	1.911	$3.14 \cdot 10^{-11}$	4.15
	2-methylpropene	56	1.117	2.890	$5.11 \cdot 10^{-11}$	11.37
	1-pentene	70	1.852	2.157	$3.14 \cdot 10^{-11}$	3.81
	1.3-butadiene	54	1.644	1.711	$6.65 \cdot 10^{-11}$	6.19
Higher aromatics	ethylbenzene	106	0.533	1.111	$7.00 \cdot 10^{-12}$	18.48
	1.2.3-trimethylbenzene	120	2.883	3.189	$3.27 \cdot 10^{-11}$	5.01
	1.2.4-trimethylbenzene	120	2.758	2.999	$3.25 \cdot 10^{-11}$	18.45
	1.3.5-trimethylbenzene	120	2.554	2.969	$5.67 \cdot 10^{-11}$	6.75
	styrene	104	0.942	0.987	$5.80 \cdot 10^{-11}$	4.14
Others	1-propanol	60	0.949	1.476	$5.82 \cdot 10^{-12}$	4.79
	2-propanol	60	0.192	1.935	$5.09 \cdot 10^{-12}$	8.44
	1-butanol	74	1.166	1.728	$8.48 \cdot 10^{-12}$	5.63
	2-butanol	74	0.683	2.099	$8.70 \cdot 10^{-12}$	4.05
	methyl acetate	74	0.115	1.661	$3.49 \cdot 10^{-13}$	4.66
	ethyl acetate	88	0.462	1.823	$1.68 \cdot 10^{-12}$	13.72
	butyl acetate	116	0.615	2.469	$4.92 \cdot 10^{-12}$	6.88
	4-methyl-2-pentanone	100	1.770	3.759	$1.41 \cdot 10^{-11}$	11.73