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An expanded DMS multiphase scheme in TM5-MP:

the importance on the OCS global budget

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Introduction

- Marine dimethyl sulfide (DMS; CH₃SCH₃) accounts for >50 % of natural gas-phase sulfur emissions, however, its oxidation mechanism is still not well understood.
 - Methanesulfonic acid (MSA;CH₃SO₃H) is efficiently formed via the multiphase OH-addition DMS oxidation pathway.
- The oxidation of DMS is also an essential indirect source of the long-lived carbonyl sulfide (OCS), the most abundant atmospheric sulfur gas that largely controls the stratospheric aerosol loading and is used as a climate diagnostic due to its close coupling to the biospheric uptake of CO₂.
 - Theoretical and laboratory studies have proposed that under <u>pristine conditions</u> the DMS H-abstraction oxidation products may undergo a series of rapid intramolecular H-shift isomerization reactions, yielding the stable intermediate hydroperoxy-methyl thioformate (HPMTF; HOOCH₂SCHO) that can lead to OCS formation.

Objectives

- Global/regional CTMs often simplistically describe the DMS oxidation processes, neglecting the role of multiphase chemistry and other intermediates found in chamber and field studies (e.g., Hoffmann et al., 2016; Wu et al., 2015).
- □ For this, we here expand the chemistry scheme in TM5-MP to account for:
 - a. the gas-phase DMS oxidation via:
 - □ the OH-addition pathway
 - the H-abstraction pathway
 - the isomerization branches
 - b. the aqueous-phase DMS oxidation in:
 - cloud droplets
 - aerosol water



Model configuration

- TM5-MP is employed here on a low global horizontal resolution of 6°×4° (25 hybrid layers).
- The standard **DMS** mechanism has been replaced with an **explicit oxidation scheme**, both in the gaseous and aqueous phases.
- The OCS and CS₂ atmospheric chemistry schemes are also included in the model:
 - The **positive fluxes** of OCS (biomass burning, anthropogenic, oceanic) and CS₂ (anthropogenic, oceanic) (Ma et al., 2021) are considered as emission rates in TM5-MP.
 - The OCS **negative fluxes** (i.e., soil, vegetation, ocean; Ma et al., 2021), are converted online into deposition rates (m/s).
- Global simulations (2000-2005) are performed, using initial concentrations for OCS from Ma et al. (2020)'s posterior simulation (*the first 5 years were used as a spin-up period*).
- **KPP** is used to generate the numerical integrations of the gas and aqueous chemical mechanisms.









The TM5-MP DMS chemistry scheme

- ❑ The standard TM5-MP chemistry schemes (i.e., *mCB05, MOGUNTIA*) contain three gas-phase DMS oxidation reactions, i.e.:
 - $\square \quad DMS + OH \rightarrow SO_2 (i.e., the H-abstraction pathway)$
 - \square DMS + OH \rightarrow 0.75 SO₂ + 0.25 MSA (i.e., the OH-addition pathway)
 - $\square \quad DMS + NO_3 \rightarrow SO_2 + \overline{H}NO_3 \text{ (nocturnal)}$
- The new representation of DMS oxidation explicitly describes:
 - the chemical evolution of DMS oxidation products via the
 H-abstraction and OH-addition pathways,
 - the MSA production in the gas and aqueous phases,
 - the HPMTF production via isomerization reactions, and
 - The **OCS** formation via HPMTF oxidation.



image courtesy: Fung et al., Atmos. Chem. Phys., 2022

Results: MSA



Budget terms (Gg S yr ⁻¹)	New DMS	Old DMS	
Chemistry Production (%aer)	1175.9 (78%)	2141.7 (100%)	
• $MSA(g) \rightarrow MSA(aq)$	326.9		
> $MSIA(g) + OH(g)/O_3(g)$	153.6 (gas)		
\succ $CH_3SO_2(g) + OH(g)/HO_2(g)$	425.9 (gas)		
• MSIA(aq) + O ₃ (aq)/OH(aq)	596.4		
• $CH_3SO_2(aq) + OH(aq)/ROx(aq)$	0.08		
• DMS + OH \rightarrow	-	2141.7	
Chemistry Destruction	15.3 (total)	-	
• Destruction by OH(g)	3.8		
• Destruction by OH(aq)	11.5		
Deposition (%wet)	1117.8 (96%)	2080.2 (98%)	
• gas.	105.9		
• aer.	911.9	2080.2	
Global Burden	25.2	43.8	
• gas.	6.75		
• aer.	18.45	43.8	
Lifetime (days)	8.9	7.7	



ż

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HPMTF (ppt)

8

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HPMTF concentrations may be as high as 50% of the DMS concentrations, but this species was an **unknown** until recently (Veres et al., 2021) !

The TM5-MP OCS/CS₂ chemistry scheme

- ...via carbon disulfide (CS₂) photo-oxidation $CS_2 + hv/O(^{3}P)/OH/NO_3 \rightarrow 0.83 \text{ OCS} + 0.17 \text{ CO} + 1.17 \text{ SO}_2 (+ HNO_3)$
- ...via DMS oxidation {H-abstraction pathway}
- 1) HPMTF ($HOOCH_2SCHO$) isomerization branch according to Wu et al. (2015) theoretical calculations: HPMTF + OH \rightarrow HPMSCO (HOOCH_2SCO) + H₂O HPMSCO \rightarrow HOOCH₂S + CO (fast) HPMSCO \rightarrow OH + CH₂O + OCS (slow) -{isomerization}
- a prompt OCS production via HPMTF oxidation according to Jernigan et al. (2022) chamber experiments: HPMTF + OH → 0.13 OCS + 0.87 SO₂ + products {lumpled reaction}
- 3) via the thioformaldehyde $(H_2C=S)$, based on Barnes et al. (1994; 1996; 2006) and Albu et al. (2008) DMS + OH $\rightarrow \dots \rightarrow$ CH₃S (methylthiyl radical) + O₂ CH₃S + O₂ $\rightarrow H_2C=S$ $H_2C=S$ + OH/hv \rightarrow OCS + H₂O
- ...destruction OCS + $hv/O(^{3}P)/OH/NO_{3} \rightarrow SO_{2} + CO_{2} (+ HNO_{3})$

Current

understanding of

OCS chemistry

production cannot explain observations!!!

Is there a another source of OCS in the atmosphere?

- Wu et al. (2015) theoretical calculations indicated the production of OCS via the **isomerization** of the HPMTF oxidation products...
- Jernigan et al. (2022) also proposed that **HPMTF gas-phase oxidation** is a good candidate for closing the OCS atmospheric budget, although current understanding of the chemistry is still limited...
- Ma et al. (2021) inverse modeling study indicated
 432 Gg S yr⁻¹ of OCS missing source to obtain a good fit of TM5-4DVAR with the NOAA observations. This "unknown" OCS source is likely:
 - located in the tropical regions,
 - showing a seasonal variation, but
 - not an important year-to-year variation.





Maarten's speculation...

- **Q:** Is it possible OCS to be produced aloft, such as in the tropical cloud layer?
- A: We don't know; no experimental or theoretical data exist yet to confirm or reject such aqueous-phase chemistry...



But, how could that chemistry be, and what would be the impact on OCS concentrations ???







A potential OCS aqueous-phase production scheme

- HPMTF is highly soluble (H = 1.33 x 10⁴ 7.96x10⁸; de Jonge et al., 2021) and is rapidly oxidized in the aqueous phase (i.e., K_{OH} = 10¹⁰ M⁻¹ s ⁻¹; de Jong et al., 2021):
 - HOOCH₂-S-C(OH)₂ + OH(aq) \rightarrow HO-OCH₂-S-C.-OH + H₂O (very fast)
- That hydrated radical product should be rather unstable and, like other aqueous diol-type alkyl radical species, could possibly follow rearrangement reactions via a protonation-dehydration-deprotonation/isomerization sequence (e.g., Schaefer et al., 2015):



Assuming a saturated oxygen concentration in the atmospheric aqueous phase of 2.6 × 10⁻⁴ M and a first-order rate constant of 1.8 × 10⁶ s⁻¹ (i.e., that of 2-methylbutane-2,3-diol; see Table 3 in Herrmann et al., 2015), a second-order reaction rate of K₀₂ = 3.27 × 10⁹ M⁻¹ s⁻¹ can be derived (i.e., *under variable aqueous O₂ concentrations*):

• $\text{HO-OCH}_2\text{-S-C.-OH} + \text{O}_2(\text{aq}) \rightarrow \text{products {e.g., CH}_2O(\text{aq}) + S(VI)} (fast under high O_2 concentrations)$

- The rate constant of the acid-catalyzed dehydration reaction can be respectively derived based on Schaefer et al. (2015) calculations (K_{pH} = 2.7 x 10⁵ @ pH = 2) (i.e., assuming here an exponentially pH-dependent):
 - HO-OCH₂-S-C.-OH + H⁺ \rightarrow CH₂O(aq) + O=C=S(aq) + HO⁻ (fast under low O₂ concentrations and low pH)

Results: OCS budget breakdown



Budget terms (Gg S yr ⁻¹)	This work*	Ma et al. (2021)#	
Direct OCS fluxes	375	331	
Direct flux from oceans	80	40 (net)	
Direct anthropogenic flux	148	155	
Biomass burning flux	147	136	
Indirect OCS fluxes	938	863	
Indirect COS flux via CS ₂	360	269	
Indirect COS flux via DMS	151	162	
Other Sources	427 (aq)	432 (unknown)	
Total OCS Sources	1313	1194	
OCS Sinks (<i>Net</i>)	1270 (43)	1194 (-)	
Destruction by OH	120	101	
Destruction by NO ₃	111	-	
Destruction by $O(^{3}P)$	12	-	
Destruction by photolysis	22	40	
Uptake by plants, soils, oceans	1005	1053 (no ocean)	

* 2005

2000-2012

Results: OCS evaluation





- based on Barnes et al. (1996)
- OCS production via CS₂, DMS (Barnes et al., 1996)
 & HPMTF in the aqueous phase (this work)
- OCS production via CS₂ and DMS but only through HPMTF oxidation in the gas phase (based on Jernigan et al. 2022)

Conclusions

- 1. A detailed DMS oxidation scheme in TM5MP leads to **much lower MSA production** than the standard scheme used in the model. Although model evaluation is likely being improved, the bulk approach for MSA applied in TM5MP limits the comparison to available observations.
- 2. HPMTF model evaluation shows a better skill when a **faster k(OH)** rate (i.e., Vermeuel et al., 2020) is used in the model compared to the experimentally derived rate from Jerningan et al. (2002).
- **3.** CS₂ oxidation is an essential driver of OCS production in the model, however **much higher** compared to inverse modeling estimates (probably due to a higher OH production?).
- **4.** The "*classic*" OCS production pathway from the DMS oxidation (i.e., ~0.7% yield) **cannot** solely explain the observations (see Ma et al., 2021).
- **5.** On the other hand:
 - *a.* The isomerization of the HPMTF oxidation products (Wu et al., 2015) leads to **too low** OCS production (~0.5 Gg S yr⁻¹) \rightarrow severely underestimating the observations!
 - b. The prompt OCS formation (~13%) from HPMTF + OH oxidation (Jerningan et al., 2002), leads to too high production (~1415 Gg S yr⁻¹) → significantly overestimating the observations!
 - *c.* A potential aqueous phase OCS production in the model (**427 Gg S yr**⁻¹) agrees well with the "unknown field" rate (**432 Gg S yr**⁻¹) as indicated by Ma et al. (2021) and compares satisfactorily with NOAA flask observations \rightarrow such a mechanism **needs to be proven experimentally**!!!

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Thank you

Extra Slides

Global OCS Budget Calculations

Budget terms (Gg S yr ⁻¹)	Berry et al. (2013)	Ma et al. (2021)	This work (<i>HPMTFqas</i>)	This work (<i>HPMTFag</i>)
Direct OCS fluxes	239	331	375	
Direct flux from oceans	39 (net)	40 (net)	80	
Direct anthropogenic flux	64	155	148	
Biomass burning flux	136	136	147	
Indirect OCS fluxes	354	431	1041	511
Indirect COS flux via CS ₂ from oceans	81	81	360	
Indirect anthropogenic flux from CS ₂	116	188		
Indirect COS flux via DMS from oceans	156	156	681	151
Indirect anthropogenic flux from DMS	1	6		
Other Sources	601	432	-	427
OCS Sources	1194	1194	1415	1313
OCS Sinks (Net)	1194(0)	1194(0)	1312(103)	1270(43)
Destruction by OH	101	101	138	120
Destruction by NO ₃	-	-	128	111
Destruction by O	-	-	14	12
Destruction by photolysis	-	40	25	22
Uptake by plants	738	1050		
Uptake by soils	355	1053	1008	1005
Uptake by oceans				1

Global CS₂ Budget Calculations

Budget terms (Gg S yr ⁻¹)	Khan et al. (2017)	Other Studies [#]	This work
Emissions	1345	800 ± 463.8	1048
Direct flux from oceans			166
Direct anthropogenic flux			882
Sinks	1194	1194	1049
Destruction by OH	1008.76	1001	858.07
Destruction by NO ₃	-	-	7.20
Destruction by O(³ P)	2.67	-	2.23
Destruction by photolysis	0.02	-	0.02
Dry deposition	321.3	53.37	181.48
Other sinks	-	694	-
Global Burden (GgS)	10.6	17.9 ± 15.5	15.8
Lifetime (days)	2.8	7.6 ± 3.8	5.5