

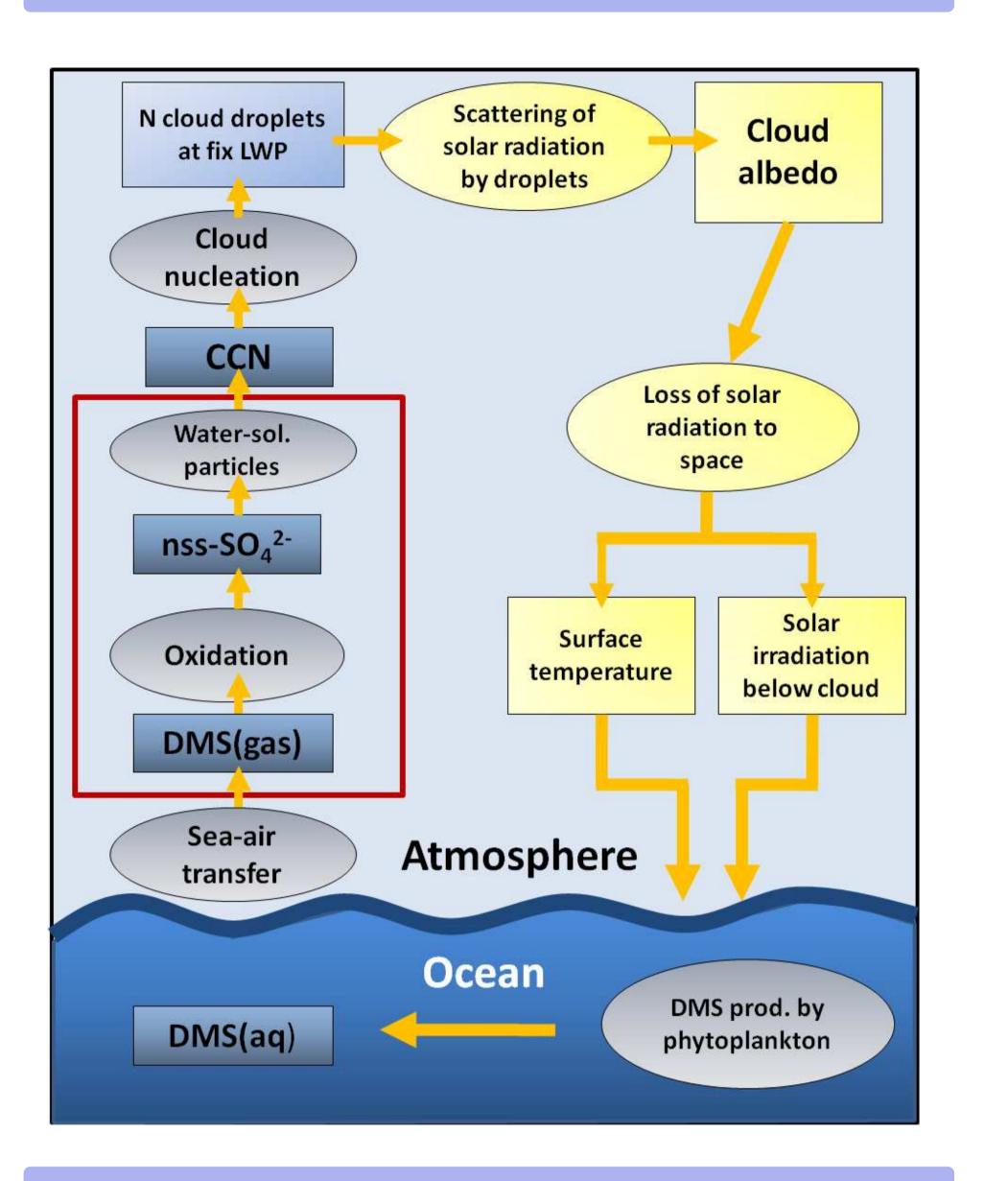
# Can Dimethyl Sulphide Cause New Particle Formation Over the Central Arctic Ocean?

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## **1. Introduction**

In summer, the central Arctic Ocean is an oceanic region nearly free from influences of continental or anthropogenic sources of sulphur gases. The formation of sulphate particles is known to take place in environments where the available aerosol surface area is low and the condensational loss of nucleating vapours is not favoured. Thus the Arctic environment seems to be ideal to test the climate feedback mechanism postulated by Charlson et al. [1] (CLAW hypothesis; see Figure below). In this study we explore the nucleation ability of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) derived from dimethyl sulphide (DMS) oxidation in the marine boundary layer (MBL) of the central Arctic Ocean.

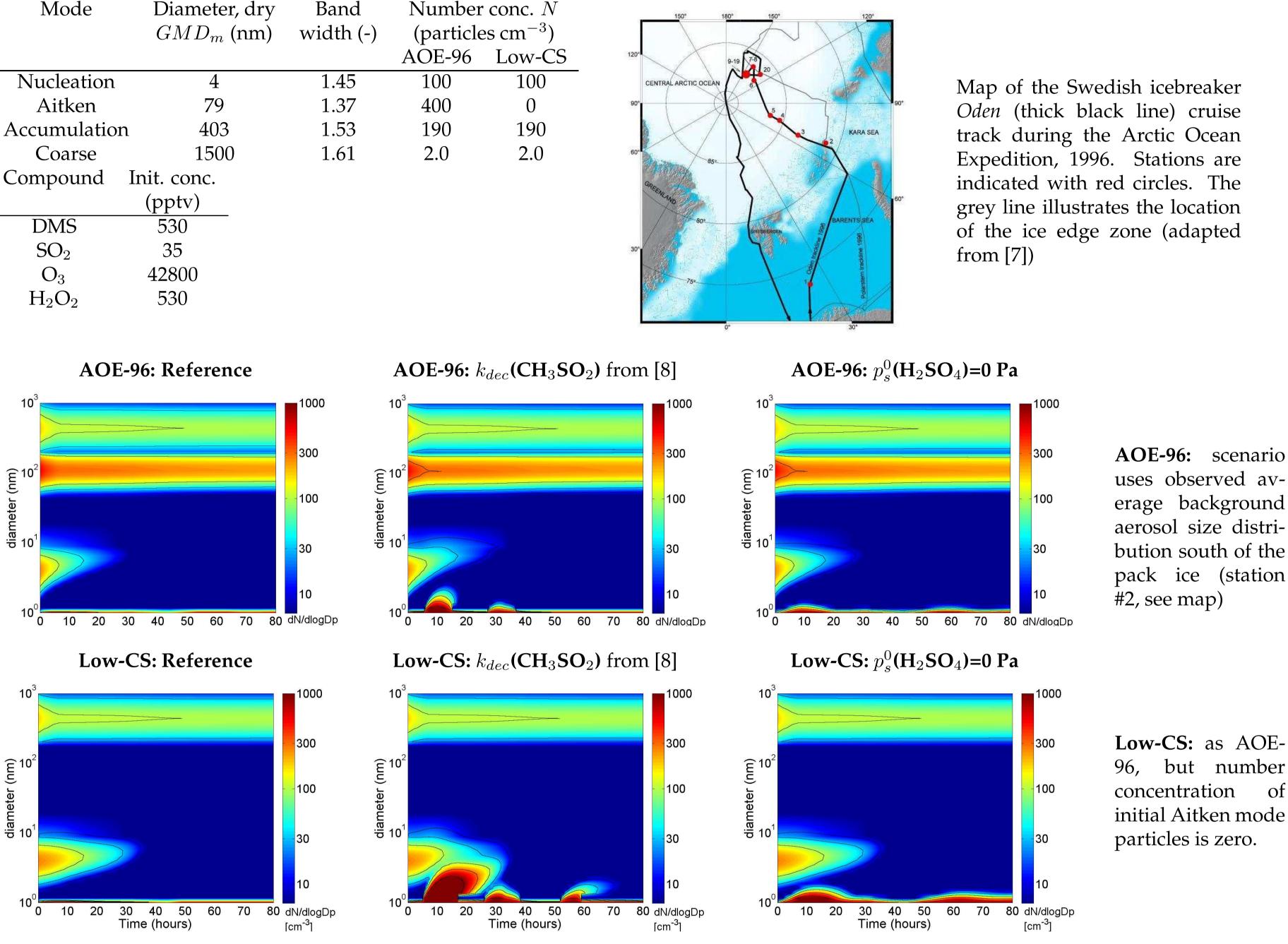


#### **4. New Particle Formation**

A marine transport scenario based on observations from the Arctic Ocean Expedition 1996 (AOE-96, see map of the icebreaker cruise) over the Arctic pack ice north of 80°N was used. Simulations (80 hours) follow an air parcel containing DMS and particles that is advected from the DMS source south of the pack ice. Nucleation is simulated using a combination of a parameterized cluster activation (nucleation rate  $J_{nucl} = A[H_2SO_4]$ , with the empirical A factor being  $2.4 \times 10^{-7} \text{ s}^{-1}$ ) and quasi steady state ion-mediated nucleation. Initial aerosol size distribution and concentrations of gas phase compounds are given in the Table below.

Scenario Table				
Mode	Diameter, dry	Band	Number conc. N	
	$GMD_m$ (nm)	width (-)	(particles $cm^{-3}$ )	
			AOE-96	Low-CS
Nucleation	4	1.45	100	100
Aitken	79	1.37	400	0
Accumulation	403	1.53	190	190
Coarse	1500	1.61	2.0	2.0
Compound Init. conc.				
_ (pptv)				

#### **AOE-96 Cruise Map**

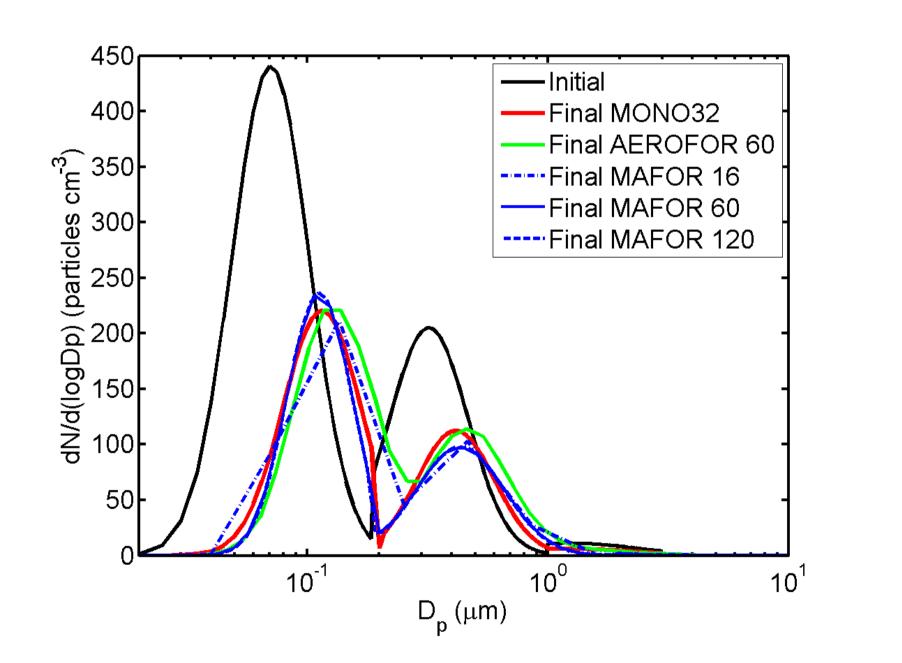




# 2. Model Description

We use the newly developed sectional multicomponent aerosol box model MAFOR which couples aerosol dynamics with photochemistry [2]. The model describes aerosol formation via different nucleation processes, growth by condensation of  $H_2SO_4$ , methanesulphonic acid (MSA) and an organic vapour (represented by succinic acid), and particle loss via coagulation, dry deposition and wet scavenging. The composition of particles in any size bin can change with time due to multicomponent condensation and/or due to coagulation. MAFOR has been evaluated against the widely applied monodisperse aerosol model MONO32 [3] and the sectional model AEROFOR [4].

For typical conditions in the MBL of the central Arctic Ocean, the model predicts that new particle formation (>3 nm) from DMS-derived sulphuric acid does not occur. The result is however sensitive to key reaction rate constants in the atmospheric DMS oxidation chain.

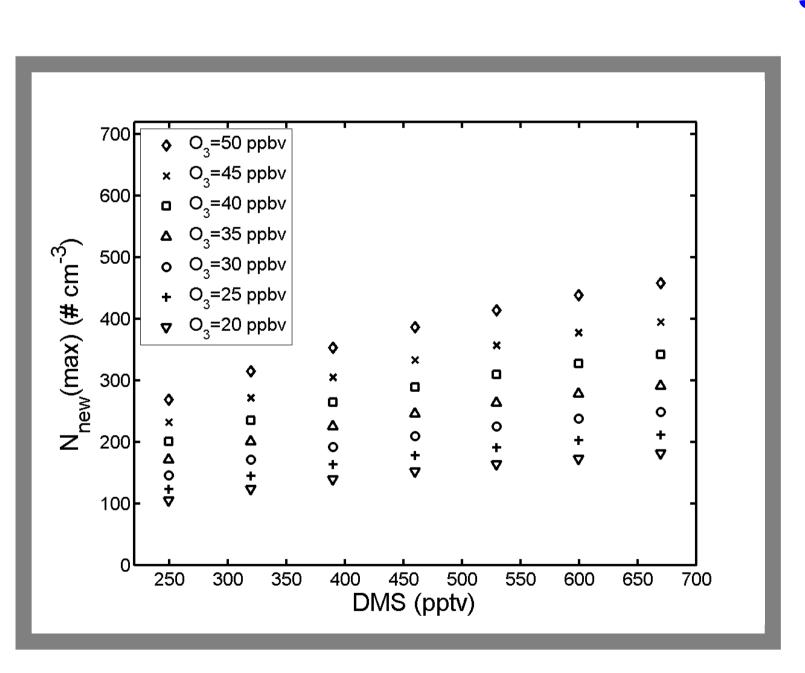


Initial (black line) and final (red line) number size distribution from MONO32 and final size distribution computed by MAFOR (blue lines) and by AEROFOR (green line) using 60 size bins.

# 3. DMS chemistry

The treatment of DMS gas phase chemistry is based on the EL CID scheme ([5], [6]). The methylsulphonyl radical, CH<sub>3</sub>SO<sub>2</sub>, is an important intermediate in DMS oxidation schemes. The rate constant of the thermal decomposition of CH<sub>3</sub>SO<sub>2</sub> is a very sensitive parameter. Its value is highly uncertain: reported values range from  $2 \times 10^{-3}$  to 500 s<sup>-1</sup> (at 280 K). It affects directly the yield of SO<sub>2</sub> and indirectly the yield of gaseous and particulate  $H_2SO_4$  and MSA.

Further, a set of 7x7 runs with a simulation duration of 52 hours was performed with MAFOR using initial DMS concentrations in the range of 250-670 pptv (steps of 70 pptv) and initial O<sub>3</sub> concentrations in the range of 20-50 ppbv (steps of 5 ppbv). Meteorological parameters were held constant (*T*=270 K, *RH*=94%, BL height: 300 m), and concentrations of DMS and O<sub>3</sub> were kept at their respective initial values. Short-lived compounds and number concentrations of new particles had reached a steady state after 24 hours. Nearly linear relationships between DMS concentrations and daily maximum total number concentrations of nucleated particles were found by the model (see Figure below).

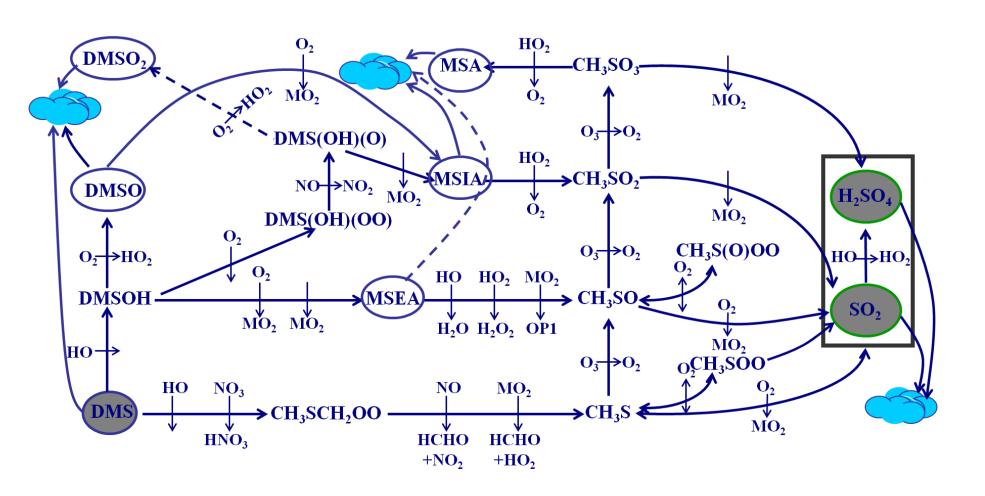


# **5.** Conclusions

- New particle formation potential of DMS-derived H<sub>2</sub>SO<sub>4</sub> was tested for a wide range of observed DMS and O<sub>3</sub> concentrations and background aerosol size distributions.
- Model simulations indicate that growth of nucleation mode particles (3-25 nm diameter) to CCN sizes under typical Arctic conditions can only occur in the presence of condensing organic vapours with sufficiently high concentrations in the gas phase (>7 pptv) [2].
- Uncertainties of modelled H<sub>2</sub>SO<sub>4</sub> gas phase concentration are propagated into modelled numbers of newly formed particles.
- The rate constant of the thermal decomposition of CH<sub>3</sub>SO<sub>2</sub> is highly uncertain with impacts on predicted new particle formation.
- There is urgent need for measurements of H<sub>2</sub>SO<sub>4</sub> and MSA gas phase concentrations in the summer Arctic MBL to better constrain their availability for nucleation and condensation processes.

# 6. Planned Model Developements

• Implementation of a primary marine source (e.g. a combined organic-inorganic sea spray function).



- Improved treatment of the liquid-solid phase transformation of sulphur compounds in aerosol droplets.
- Application of Nano-Köhler theory [9] to arctic new particle formation, via activation of stable inorganic (or mixed inorganic-organic) clusters by water-soluble organic vapours.

#### **Acknowledgements**

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## References

- [1] Charlson, R. J., Lovelock, J. E., Andreae, M. O. and Warren, S. G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate; Nature 326, pp. 655-661.
- [2] Karl, M., Gross, A., Leck, C., Pirjola, L. 2011. A new flexible multicomponent model for the study of aerosol dynamics in the marine boundary layer; Tellus B, doi:10.1111/j.1600-0889.2011.00562.x, article in press.
- [3] Pirjola, L., Tsyro, S., Tarrason, L., Kulmala, M. 2003. A monodisperse aerosol dynamics module - a promising candidate for use in the Eulerian long-range transport model. J. Geophys. Res. 108(D9), 4258, doi:10.1029/2002JD002867.
- [4] Pirjola, L. 1999. Effects of the increased UV radiation and biogenic VOC emissions on ultrafine sulphate aerosol formation; J. Aerosol Sci. 30, pp. 355-367.
- [5] EL CID 2003. Evaluation of the Climatic Impact of Dimethyl Sulphide, Final report of the EC 5FP project: Evaluation of the Climate Impact of Dimethyl Sulphide (EL CID), Project coordinator Prof. Barnes, I., Contract number: EVK2-CT-1999-00033.
- [6] Karl, M., Gross, A., Leck, C., and Pirjola, L. 2007. Intercomparison of dimethylsulfide oxidation mechanisms for the marine boundary layer: Gaseous and particulate sulfur constituents; J. Geophys. Res. 112, D15304, doi:10.1029/2006JD007914
- [7] Leck, C., Nilsson, E. D., Bigg, E. K. and Bäcklin, L. 2001. Atmospheric program on the Arctic Ocean Expedition 1996 (AOE-96): An overview of scientific goals, experimental approach, and instruments; J. Geophys. Res. 106(D23), pp. 32,051-32,067.
- [8] Kerminen, V.-M. and Leck, C. 2001. Sulfur chemistry over the central Arctic Ocean in summer: Gas to particle transformation; J. Geophys. Res. 106(D23), pp. 32,087-32,099.
- [9] Kulmala, M., Kerminen, V.-M., Anttila, T., Laaksonen, A. and O'Dowd, D. 2004. Organic aerosol formation via sulphate cluster activation; J. Geophys. Res. 109, D04205, doi:10.1029/2003JD003961