TREND EVOLUTION OF CARBONYL SULFIDE ABOVE JUNGFRAUJOCH deduced from ground-based FTIR and ACE-FTS satellite observations

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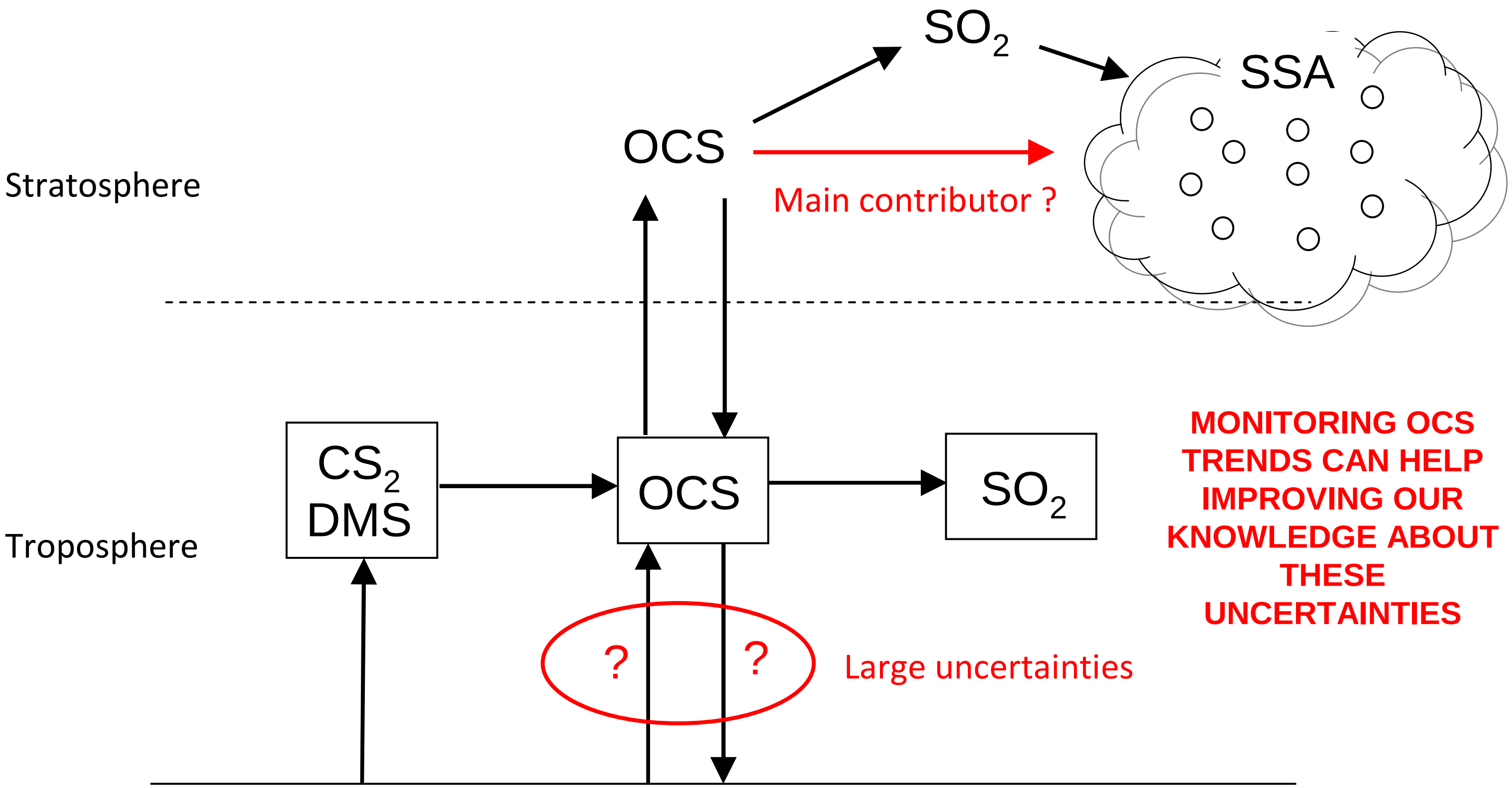
OCS

- Carbonyl sulfide (OCS) is the most abundant sulfur-containing trace gas in the atmosphere.
- Mean (free) tropospheric concentration of 465 pptv (using the HITRAN 2008 line intensities).
- Tropospheric lifetime of several years allows OCS to reach stratosphere.
- OCS is **believed*** to be the main contributor for sustaining the Stratospheric Sulfate Aerosol (SSA) layer at background levels during quiet volcanic periods (Crutzen, 1976).
- SSA influences the Earth's radiation budget and stratospheric ozone chemistry.
- "*Increasing anthropogenic emissions of OCS could cause measurable climate alterations within the next century*" (Turco et al., 1980)



MONITORING OCS TRENDS CAN HELP IMPROVING OUR KNOWLEDGE ABOUT THESE UNCERTAINTIES

*some authors have confirmed (Brühl et al., 2011), other authors have questioned this theory (Chin & Davis, 1995; Kjellstrom, 1998; Sturges et al., 2001)

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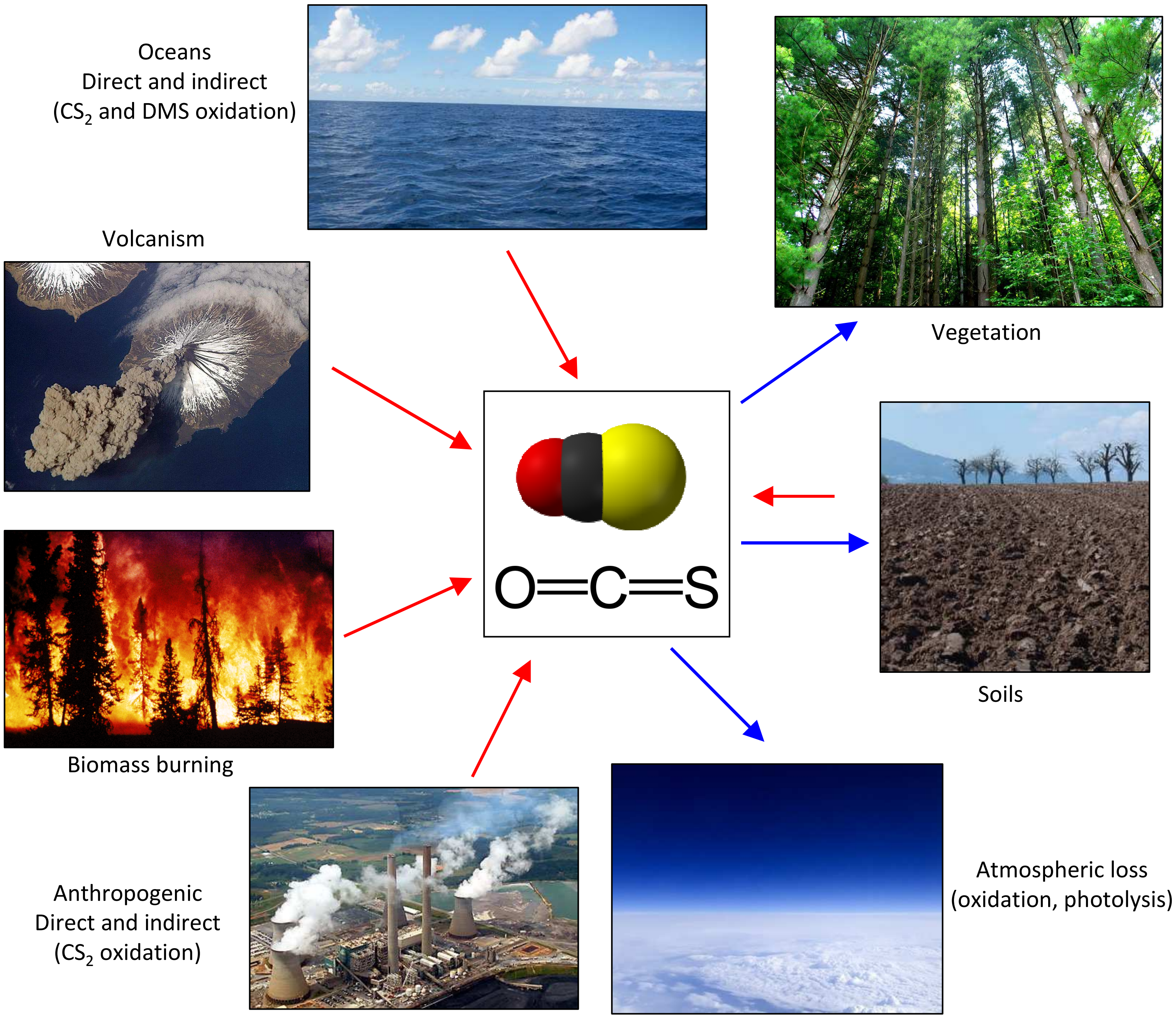

- OCS
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- Tropo
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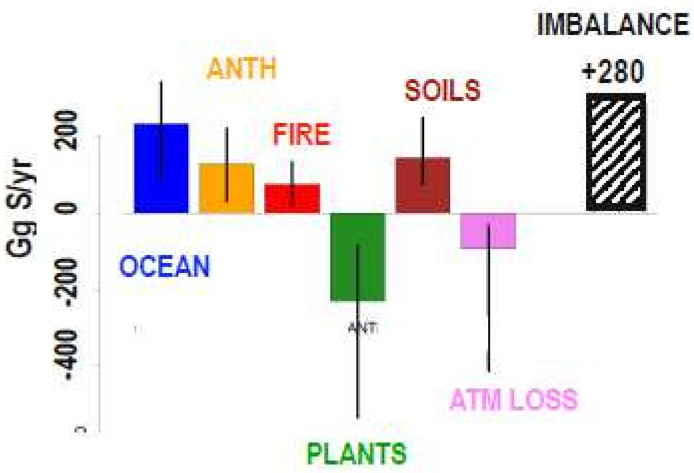
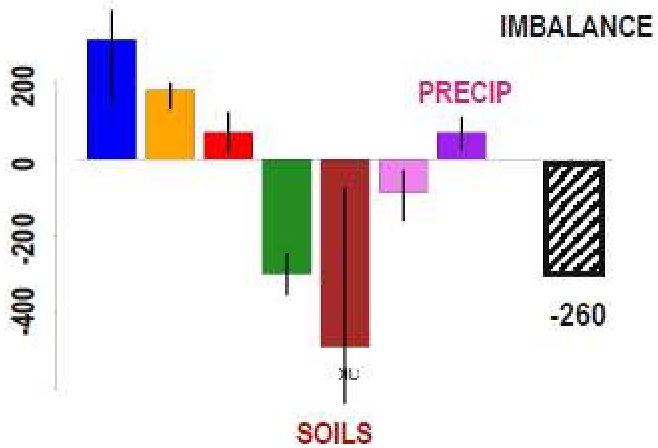
PREVIOUS GLOBAL BUDGET ESTIMATES

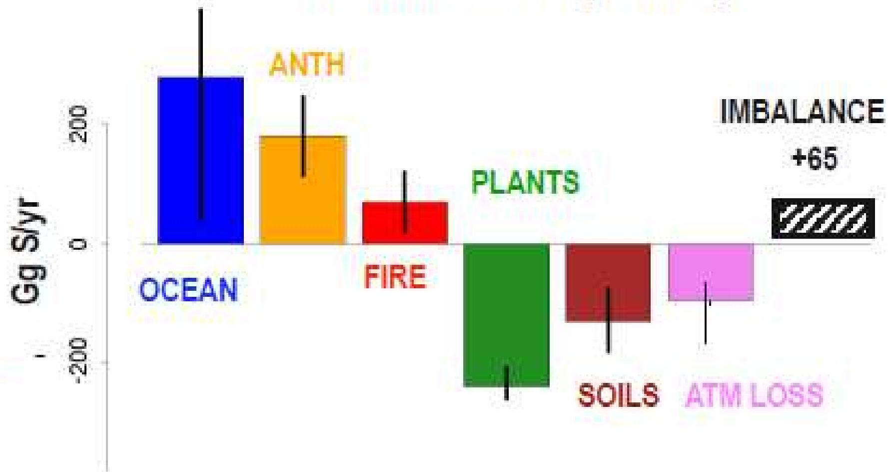
Chin and Davis 1993



Watts 2000



Kettle et al. [2002]



Extract from slides coming from P. Suntharalingam (2009)

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Table 1. Recent Estimates of Global Atmospheric COS Budget (Gg S y^{-1})

	Kettle et al. [2002] Mean (Range)[a]	*Montzka et al.* [2007] Revisions	This Study Revisions[b]
	SOURCES		
Ocean (direct and indirect)	280 (40–520)		230
Anthropogenic (direct and indirect)	180 (90–266)		
Biomass burning	70 (30–110)	68–144	
Anoxic soils and wetlands	26 (12–112)		
Total Sources	555 (170–1010)	210–1049	505
	SINKS		
Plant uptake	238 (210–270)	730–1500	490
Oxic soils	130 (74–180)		
Atmospheric loss (oxidation, photolysis)	120 (96–147)		
Total Sinks	490 (380–597)	902–1827	740

[a]Modification to K2002: biomass burning estimate is from the global total of *Nguyen et al.* [1995].
[b]Revised ocean estimate of this study is based on reductions to southern extra-tropical fluxes alone (see text).

NEW IMBALANCE - 235

Suntharalingam et al., 2008

Understimation of OCS uptake by terrestrial vegetation; some additional sources (40% of identified sources) are still missing from budget estimates

Strong seasonal correlation between OCS and CO_2 → atmospheric OCS measurements have the potential to constrain Gross Primary Production

OTHER REASON TO IMPROVE KNOWLEDGE ABOUT OCS

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FTIR DATABASE

• Fourier Transform Infrared (FTIR) spectrometer (Bruker IFS-120HR)

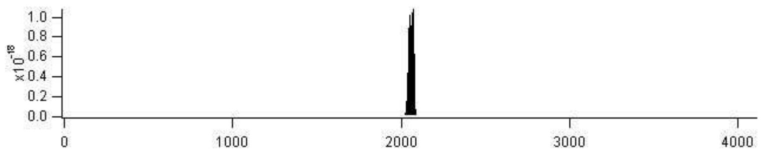
• High-altitude International Scientific Station of the Jungfraujoch (46.5°N, 8.0°E, 3580m asl)

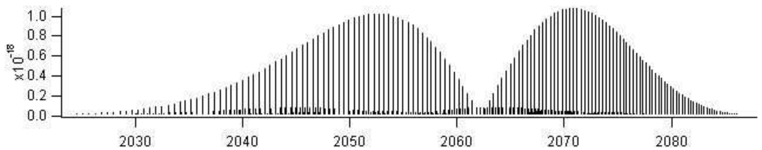
• Network for the Detection of Atmospheric Composition Change (NDACC)

Observational database used for this study:

• 4959 high-resolution (0.003 to 0.006 cm^{-1}) FTIR solar absorption spectra covering the spectral region of the strong γ_3 fundamental band of OCS centered on 2062 cm^{-1};

• regularly recorded under clear-sky conditions from January 1995 to December 2011





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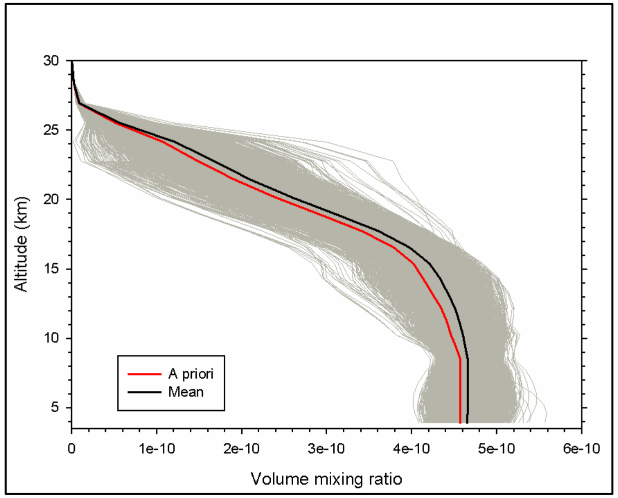
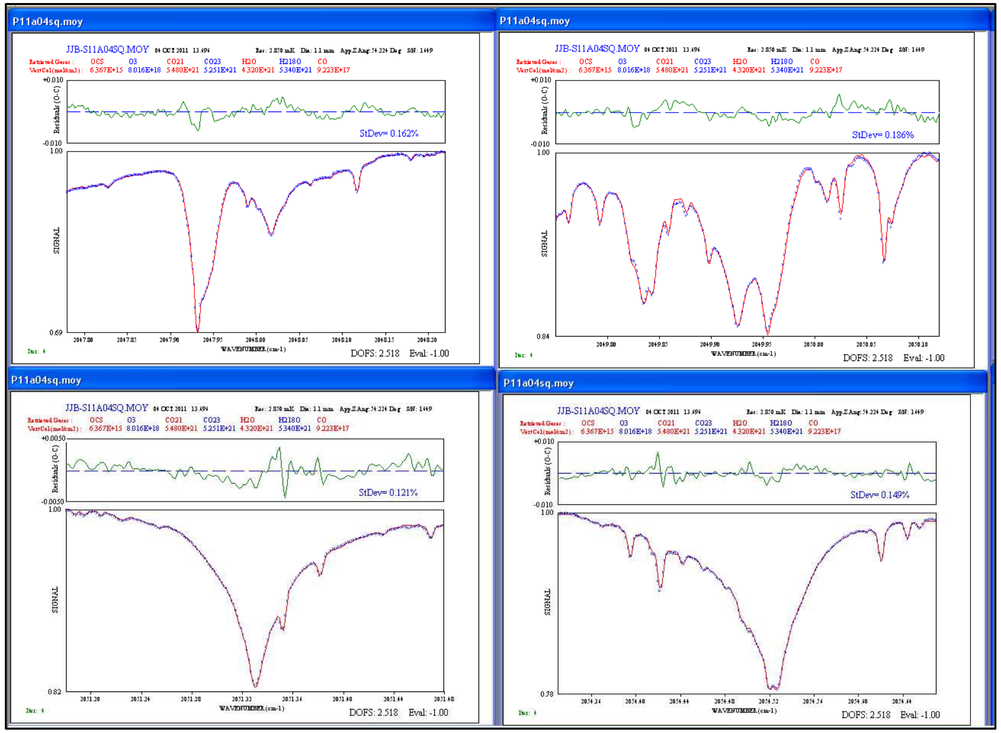
FTIR RETRIEVAL STRATEGY

New approach to retrieve atmospheric abundance of OCS from high-resolution ground-based infrared solar spectra:

- SFIT-2 v3.91 algorithm;
- HITRAN 2008 line parameters;
- 4 micro-windows covering the 2047-2055 cm^{-1} spectral region, in association with a narrow mw devoted to fit the main isotopologue of CO_2;





- major interferences : O3, CO2, H2O, CO and solar lines;
- isotopic separation for CO_2 (isotopologues 626 and 628) and H_2O (isotopologues 161 and 181);
- fitting of the vertical profile for O_3 (scaling for the others);
- a priori covariance matrix combining variability from in situ and ACE-FTS measurements

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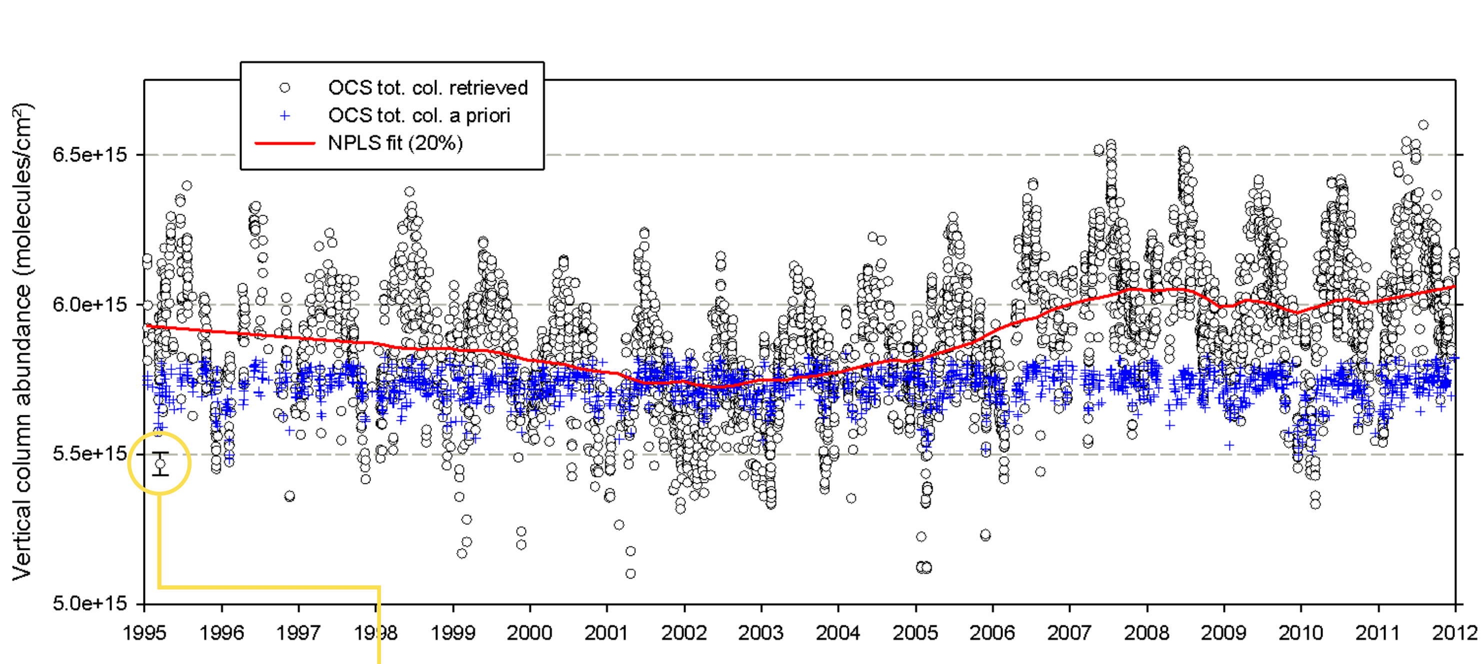
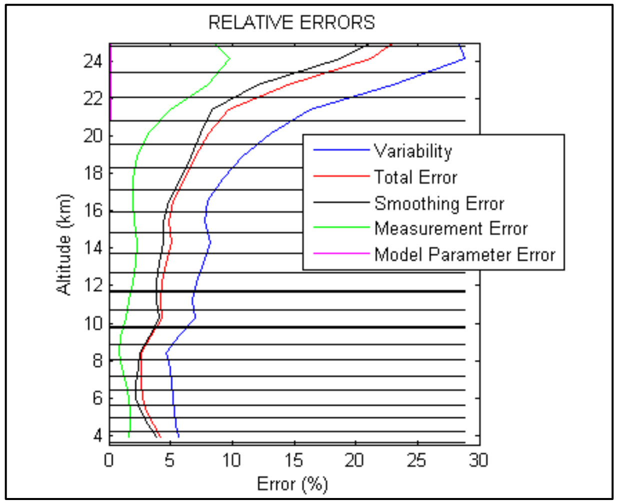
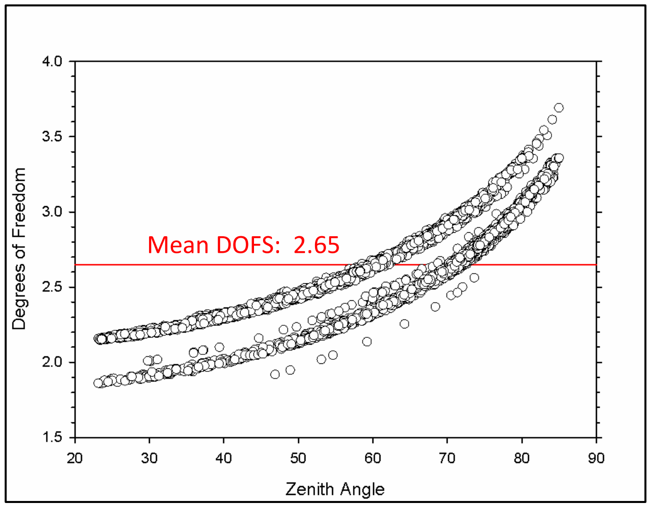
OCS ABOVE JUNGFRAUJOCH FROM FTIR MEASUREMENTS



z1	z2	Meas. Err.	Smooth. Err.	Mod. Par. Err.	Tot. Err.	Variability
3.58	100	0.57	0.4	0.03	0.69	3.77





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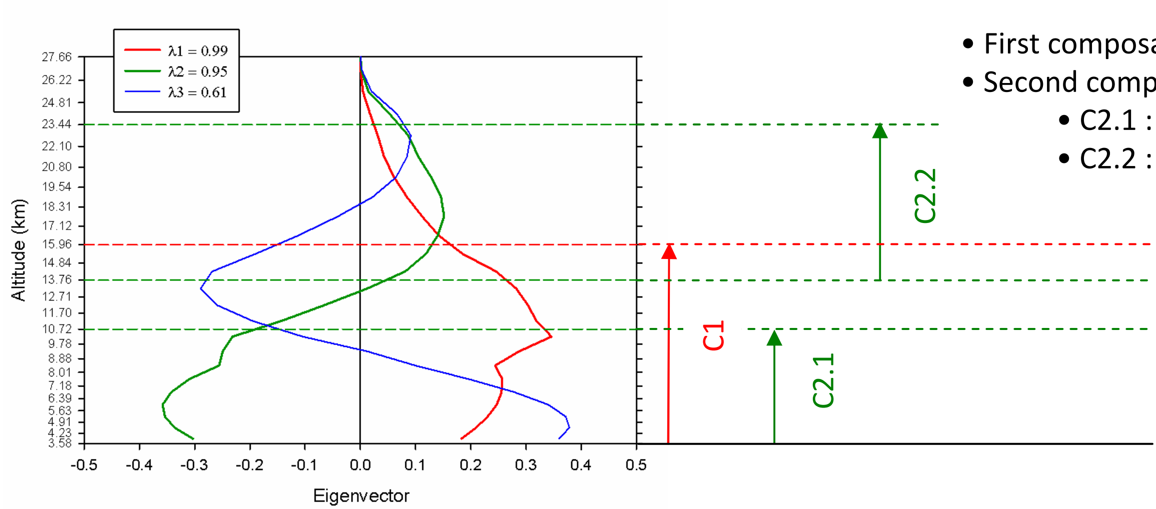
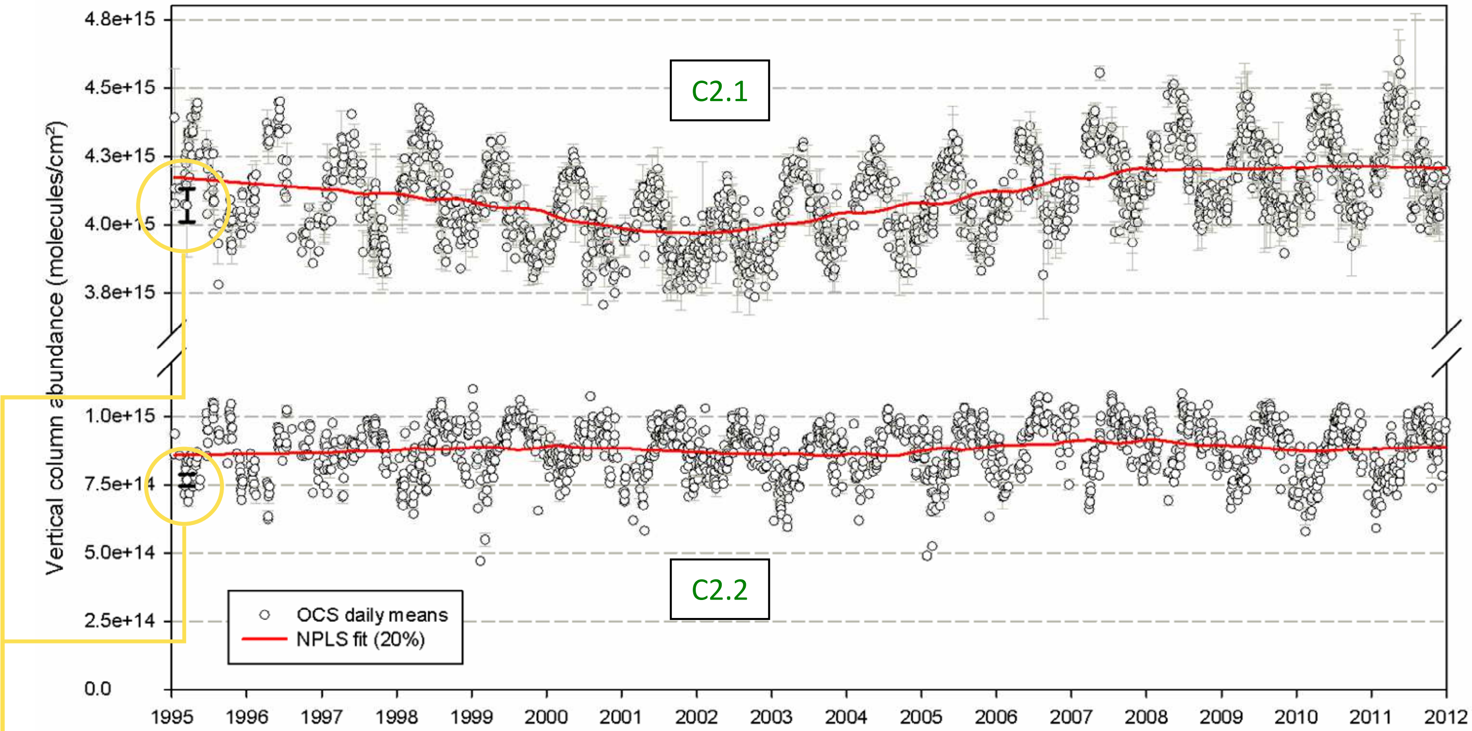
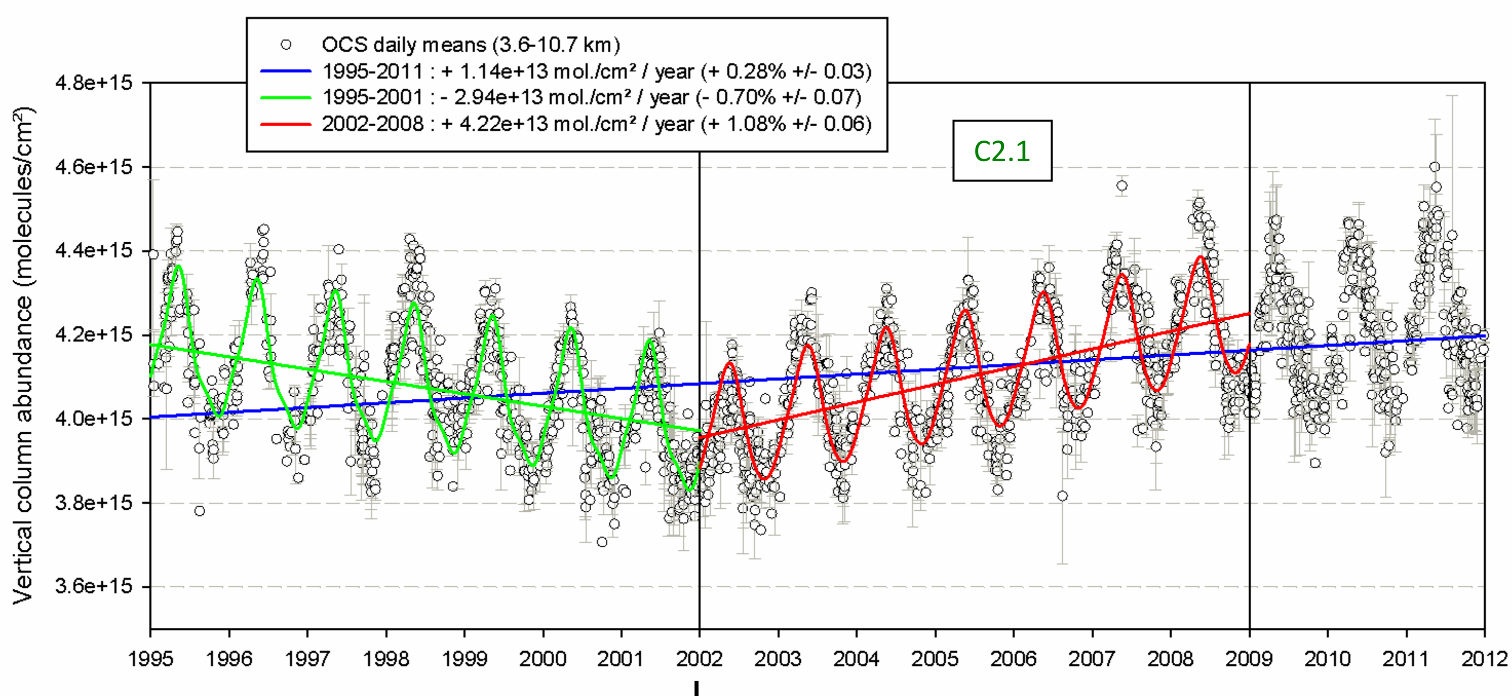


- First composant (C1) : 3.6-16 km
- Second composant :
  - C2.1 : 3.6-10.7 km (tropo)
  - C2.2 : 13.8-23.4 km (strato)

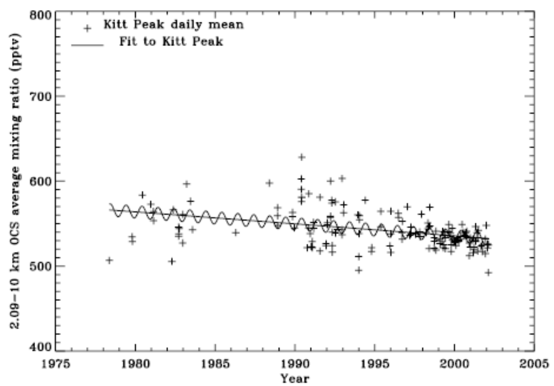


z1	z2	Meas. Err.	Smooth. Err.	Mod. Par. Err.	Tot. Err.	Variability
3.58	10.72	1.13	0.92	0.06	1.46	4.33
13.76	23.44	1.48	2.34	0.05	2.77	7.17

TROPOSPHERIC OCS ABOVE JUNGFRAUJOCH FROM FTIR MEASUREMENTS



Trend for 1995-2001 in agreement with other studies (Rinsland et al., 1998; Sturges et al., 2001; Mahieu et al., 2003; Montzka et al.,2004)



Rinsland et al., 2002

Trend for 2002-2008: to our knowledge, no one has reported about this growth period

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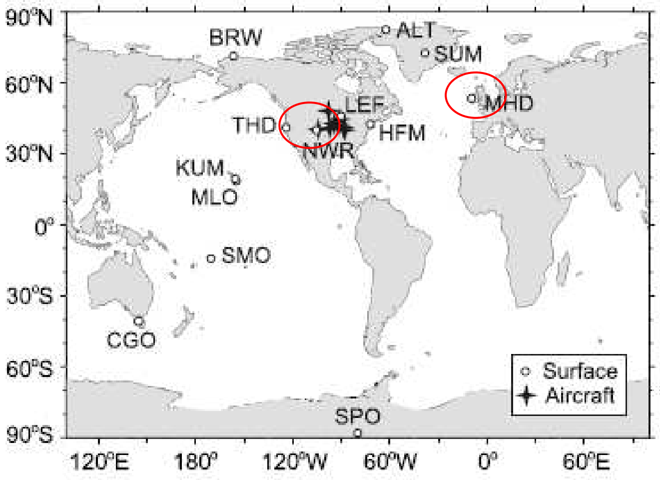
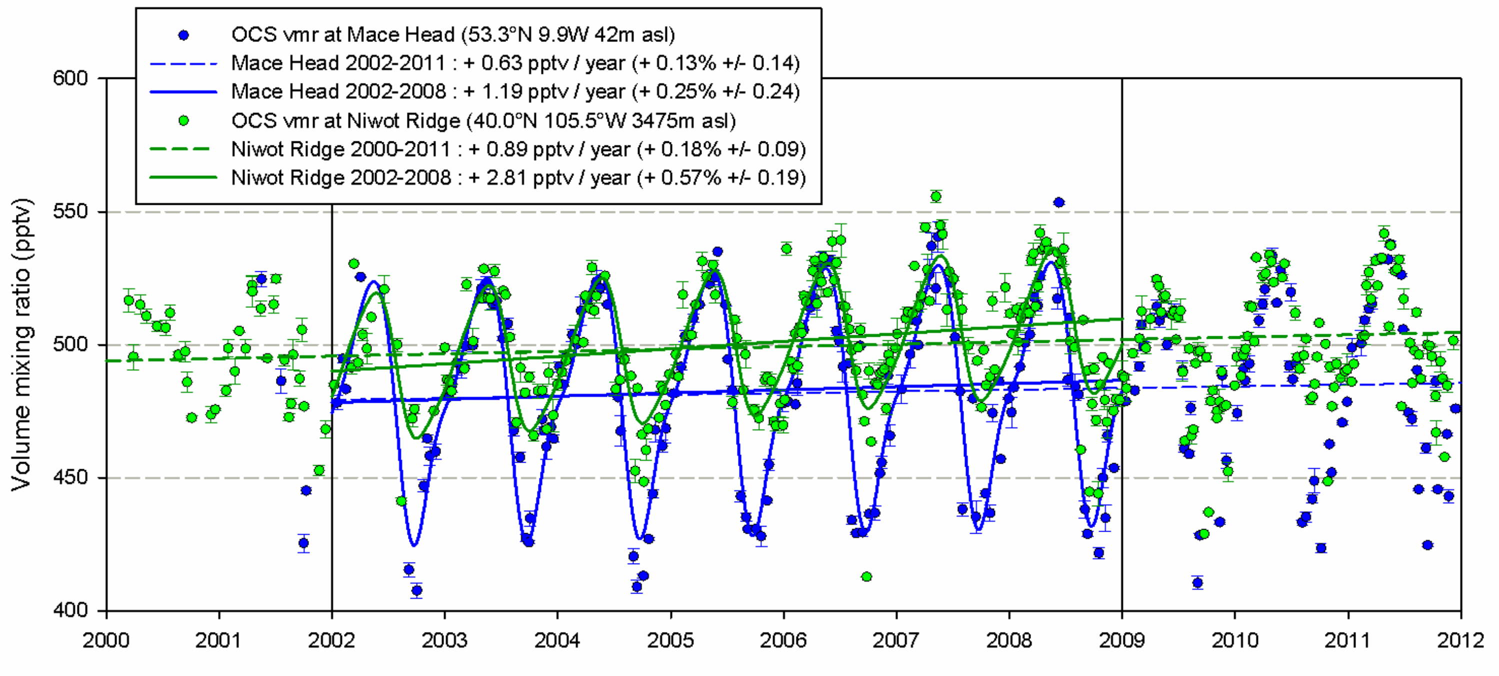
Atmospheric Measurements of OCS from the National Oceanic and Atmospheric Administration (NOAA)/Earth System Research Laboratory/Global Monitoring Division (GMD) Flask Program – Boulder, Colorado



NOAA/GMD Halocarbon Flask Network: 15 stations including:

- nwr=Niwot Ridge, Colorado, USA (40N, 105.5W, 3475 m asl) (University of Colorado site);
- mhd=Mace Head, Ireland (53.3N, 9.9W, 42 m asl);

Montzka et al., 2007



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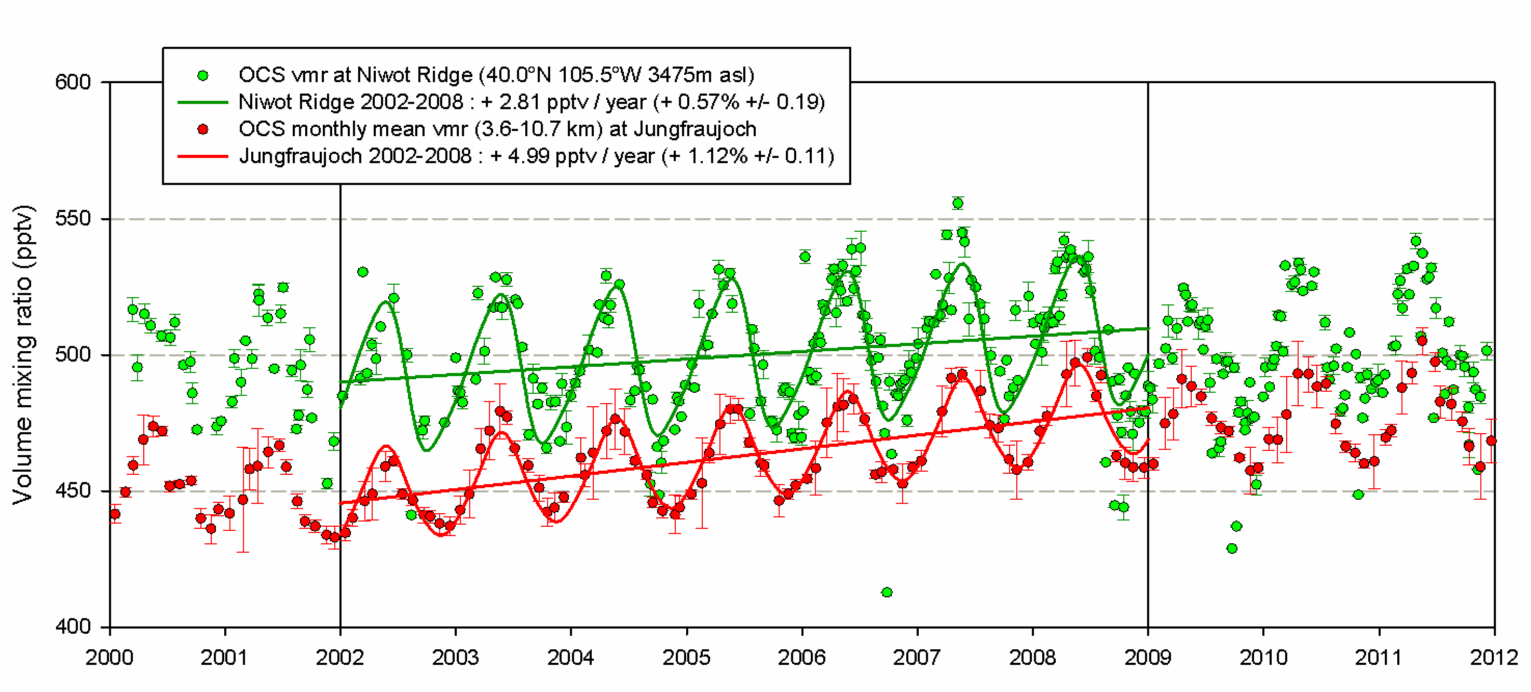
TROPOSPHERIC OCS: COMPARISON JUNGFRAUJOCH FTIR/NIWOT RIDGE IN SITU



- Specifications of Niwot Ridge site (continental localisation, latitude and altitude) are comparable with those of Jungfraujoch;
- Good agreement in terms of significant positive trend for the 2002-2008 time period;
- Relative and absolute trend values are quite different (factor of about 2 between Jungfraujoch and Niwot Ridge);
- Concentration values are lower for Jungfaujoch (air column of 7.1 km high);

- OCS
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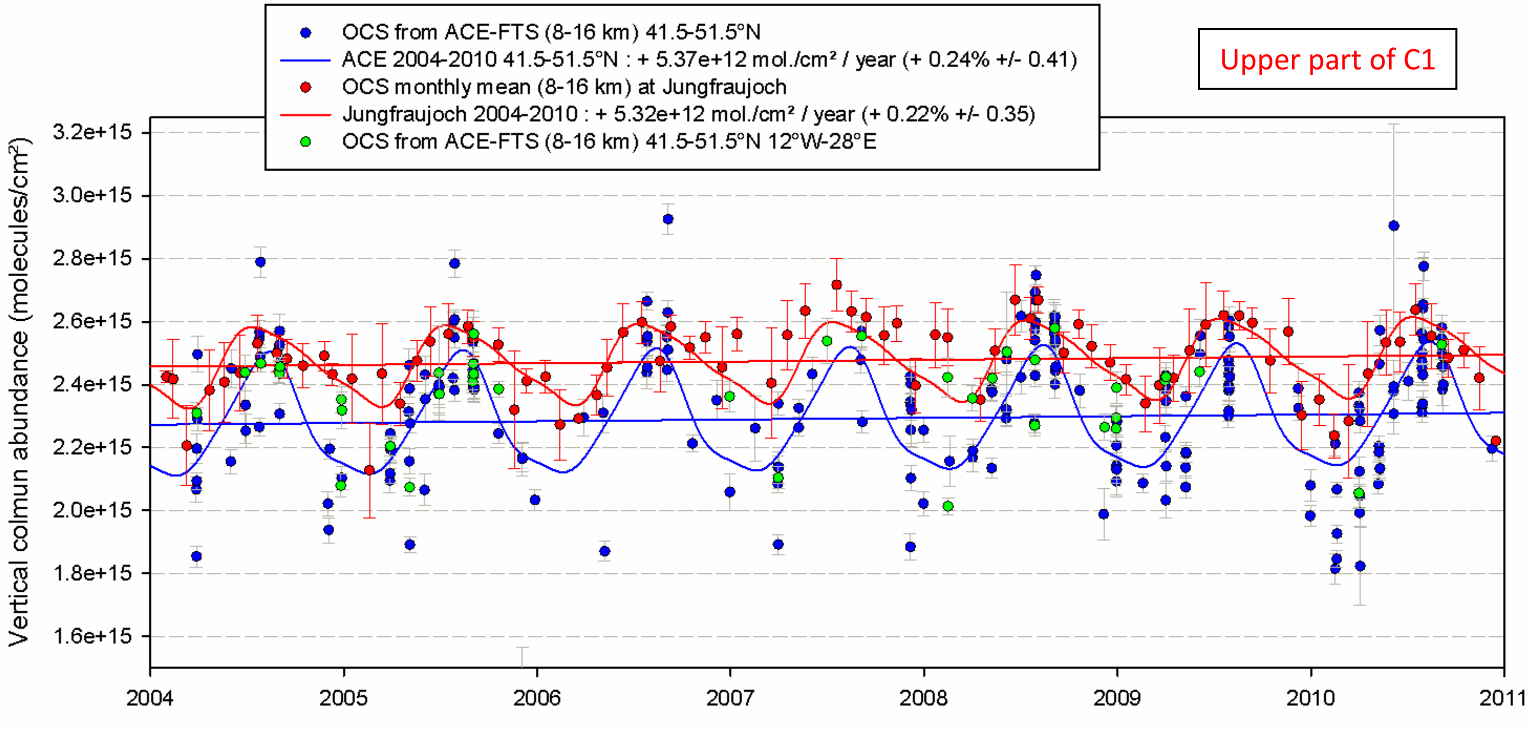
TROPOSPHERIC OCS: COMPARISON JUNGFRAUJOCH FTIR/ACE-FTS 41.5-51.5°N



- No comparison possible with ACE-FTS measurements in the C2.1 altitude range (3.6-10.7 km);
- Use of C1 upper part altitude range (8-16 km) which is the best compromise between data number and tropospheric contribution;
- Good agreement in terms of no significant trend for the 2004-2010 time period;
- Good agreement in terms of relative and absolute trend values;
- Bias of about 8% between Jungfaujoch FTIR and ACE-FTS: still to be identified.

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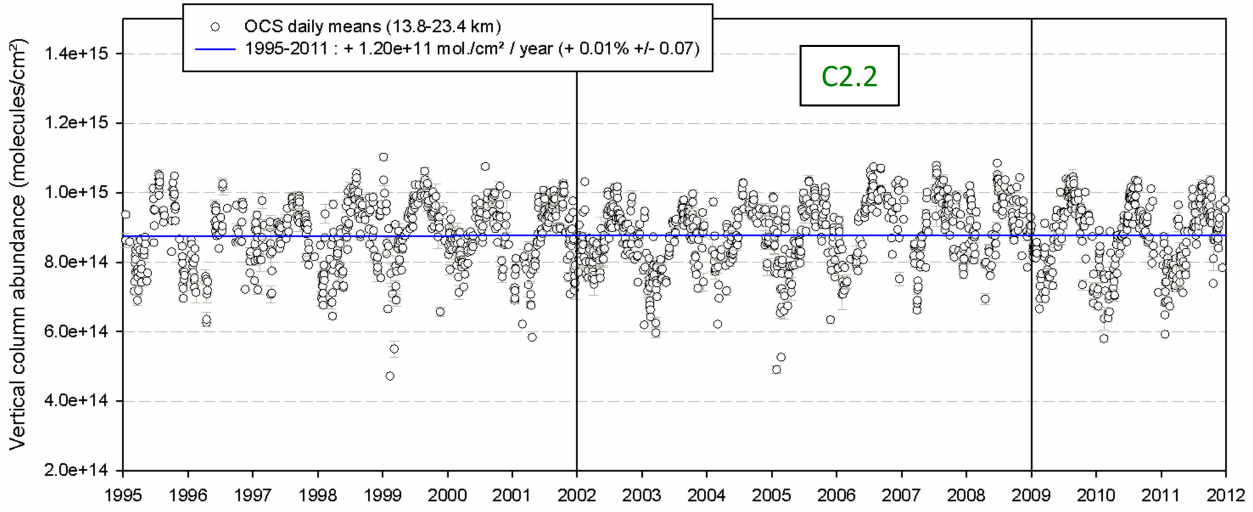
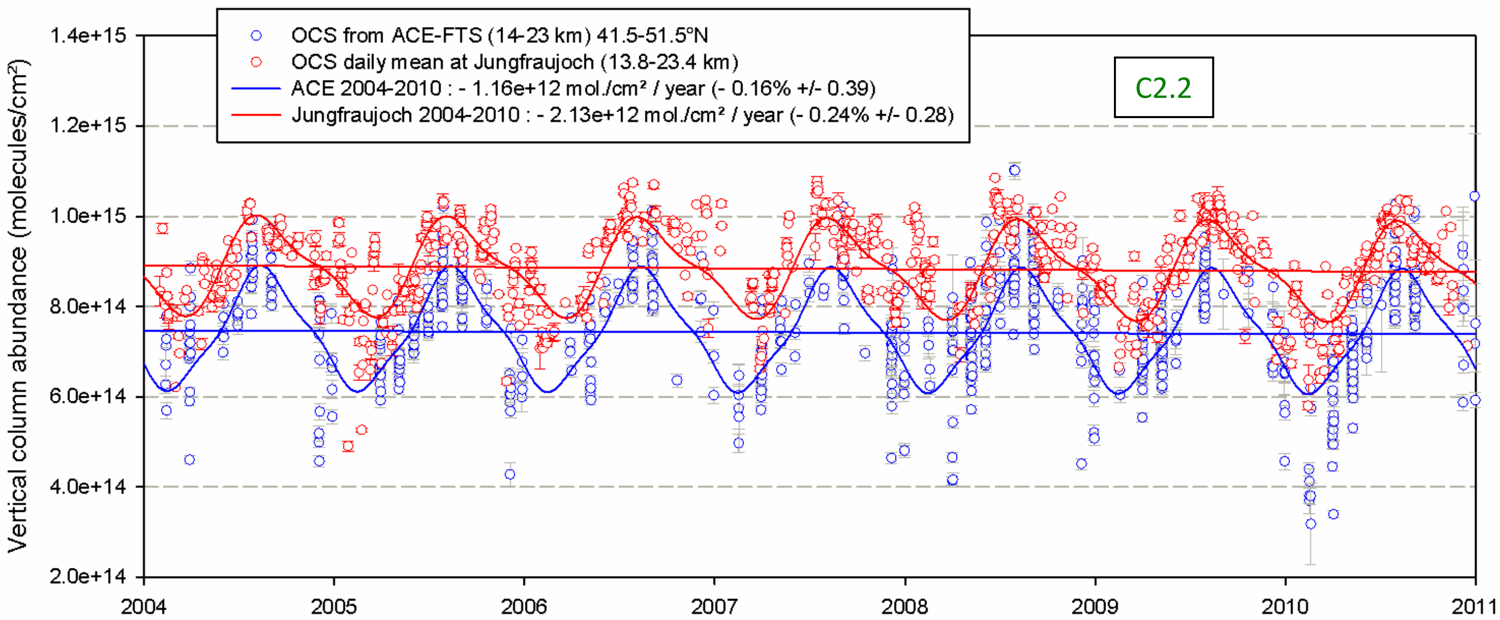
STRATOSPHERIC OCS ABOVE JUNGFRAUJOCH FROM FTIR MEASUREMENTS



STRATOSPHERIC OCS : COMPARISON JUNGFRAUJOCH FTIR/ACE-FTS 41.5-51.5°N



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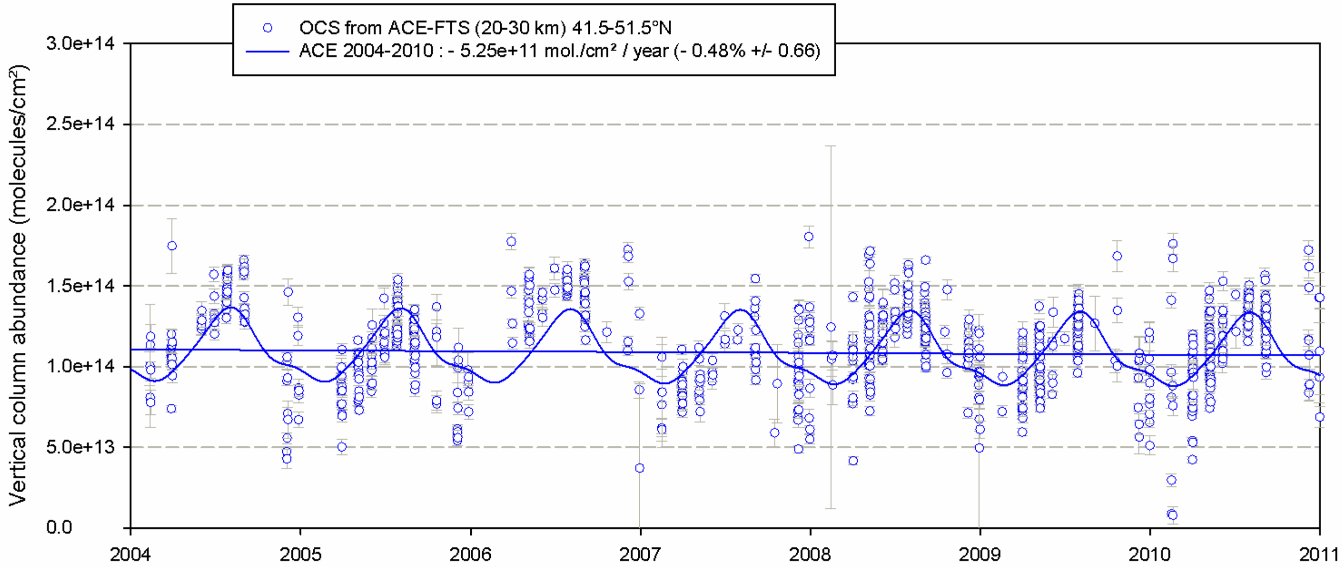
STRATOSPHERIC OCS AND SSA LAYER

• Discovery of a SSA layer containing substantial component of sulfate in the early 1960s;
• Volcanic emissions: major source;
• Presence of a persistent aerosol layer with a maximum at 20 km.

Is OCS the main contributor of sulfur during non-volcanic period ?
If it's the case, trends of stratospheric OCS and SSA must be the same...
• NO SIGNIFICANT TREND for FTIR measurements above Jungfraujoch in the lower stratosphere (13.8-23.4 km);
• NO SIGNIFCANT TREND for ACE-FTS measurements (41.5-51.5°N) in the lower stratosphere (14-23 km);
and
• NO SIGNIFICANT TREND for ACE-FTS measurements (41.5-51.5°N) in the middle stratosphere (20-30 km).

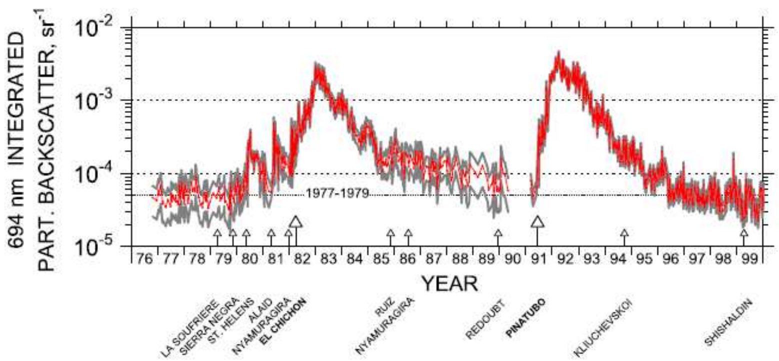


Results in agreement with recent studies:
• Coffey & Hannigan (2011): no significant trend for total column above 200hPa (30-60°N - 1978-2005) measured by airborne infrared spectrometer;
• Rinsland et al. (2008): no significant trend in lower stratosphere (30-100 hPa) at 25-35°N from ATMOS 1985/1994 and ACE 2004-2007.

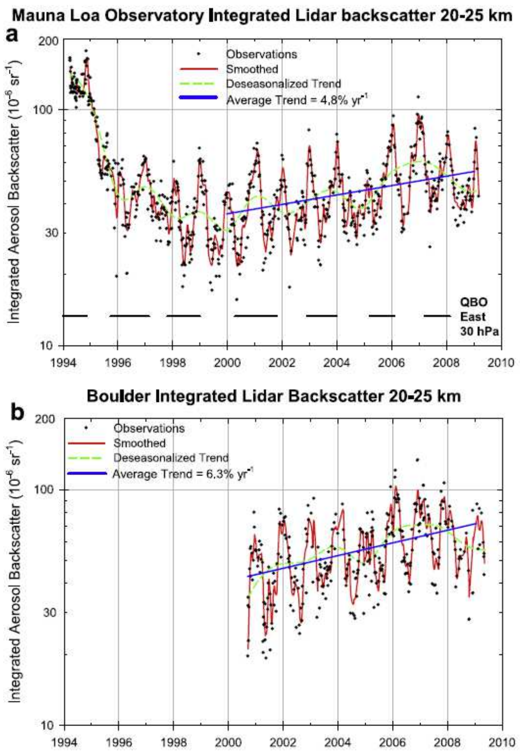
What about the evolution of SSA layer ?

→ after eruption of Mount Pinatubo (1991), SSA background level reached between 1998 and 2002;

Jäger, 2005

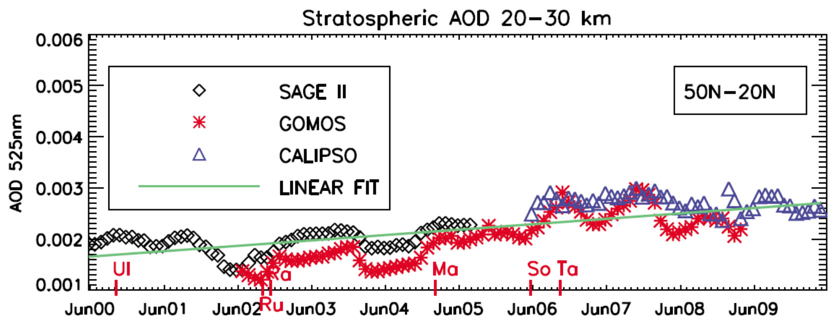


Hofmann et al., 2009



BUT... since 2002: <u>systematic increase of the SSA level</u>;
No consensus in the literature to explain this evolution:

- Hofmann et al. (2009): increase of coal burning in China since 2002 → increase of SO_2 in stratosphere;
- Vernier et al. (2010): series of moderate but intense volcanic eruptions at tropical latitudes and transfer of sulfur particles by the Brewer-Dobson circulation to higher latitudes.



Vernier et al., 2011

→ recent trend evolution of SSA layer suggests that stratospheric OCS plays a minor role in the maintain of the SSA background level.

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DISCUSSION ABOUT OCS ANTHROPOGENIC EMISSIONS

- OCS measurements coming from firn air and ice core suggest that OCS levels of the late 20th century are significantly larger than the preindustrial levels (Aydin et al., 2008) → importance of anthropogenic emissions;
- OCS interhemipheric ratio of 1.12+/-0.07 (Deutscher et al., 2008) → importance of anthropogenic emissions.

1. Oxidation of industrial CS_2 (17% of global emissions)
2. Direct anthropogenic emissions (9%)
3. Biomass burning (5%)

TOTAL for anthropogenic sources : **31%**

GLOBAL level

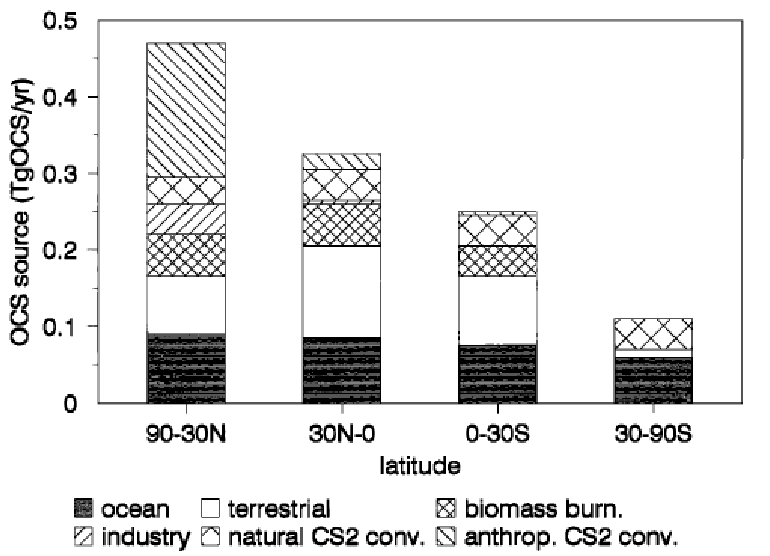
Watts, 2000

1. Oxidation of industrial CS_2 (32% of NH emissions)
2. Direct anthropogenic emissions (17%)
3. Biomass burning (6%)

TOTAL for anthropogenic sources : **54%**

Northern Hemisphere level

Kettle et al., 2002



90-30°N level

1. Oxidation of industrial CS_2 (38% of 90-30°N emissions)
2. Biomass burning (12%)
3. Direct anthropogenic emissions (9%)

TOTAL for anthropogenic sources : **59%**

Chin&Davis, 1993

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DIRECT ANTHROPOGENIC EMISSIONS: ALUMINIUM PRODUCTION

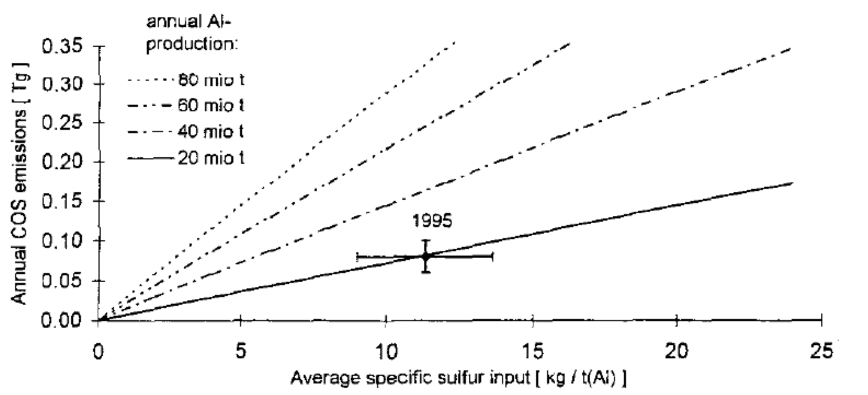
Process	Flux ($Tg\ a^{-1}$)	Comment ($Tg\ a^{-1}$)	Reference
Coal combustion	0.036 ± 0.011		Chin and Davis (1993)
Industrial S recovery	0.002 ± 0.0015		Chin and Davis (1993)
Cars	0.006 ± 0.004	Dependant on sulfur levels in fuels	Fried et al. (1992); Watts and Roberts (1999)
Aluminum production	0.08 ± 0.06	Increasing to 0.32 by 2030	Harnisch et al. (1992)
Total	0.124 ± 0.061		

Watts, 2000

→ Not mentioned by Chin&Davis (1993)

Aluminium production responsible of significant OCS emissions (Harnisch et al., 1995):
- Hall–Héroult process: major industrial process for the production of aluminium (dissolving Al_2O_3 in molten cryolite, and electrolysing the molten salt bath to obtain pure aluminium metal);
- Use of graphite cathodes and carbon anodes containing sulfur (about 2.5%);
- OCS emission estimated of 4 kg per ton Aluminium produced ;
- 1995: 20 millions tons Aluminium → 0.08 Tg OCS emitted;
- 2011: 43 millions tons Aluminium (International Aluminium Institute)

→ 0.17 Tg OCS emitted → + 74 % of direct anthropogenic emissions → + 22% for OCS anthropogenic sources → + 7% for total OCS sources



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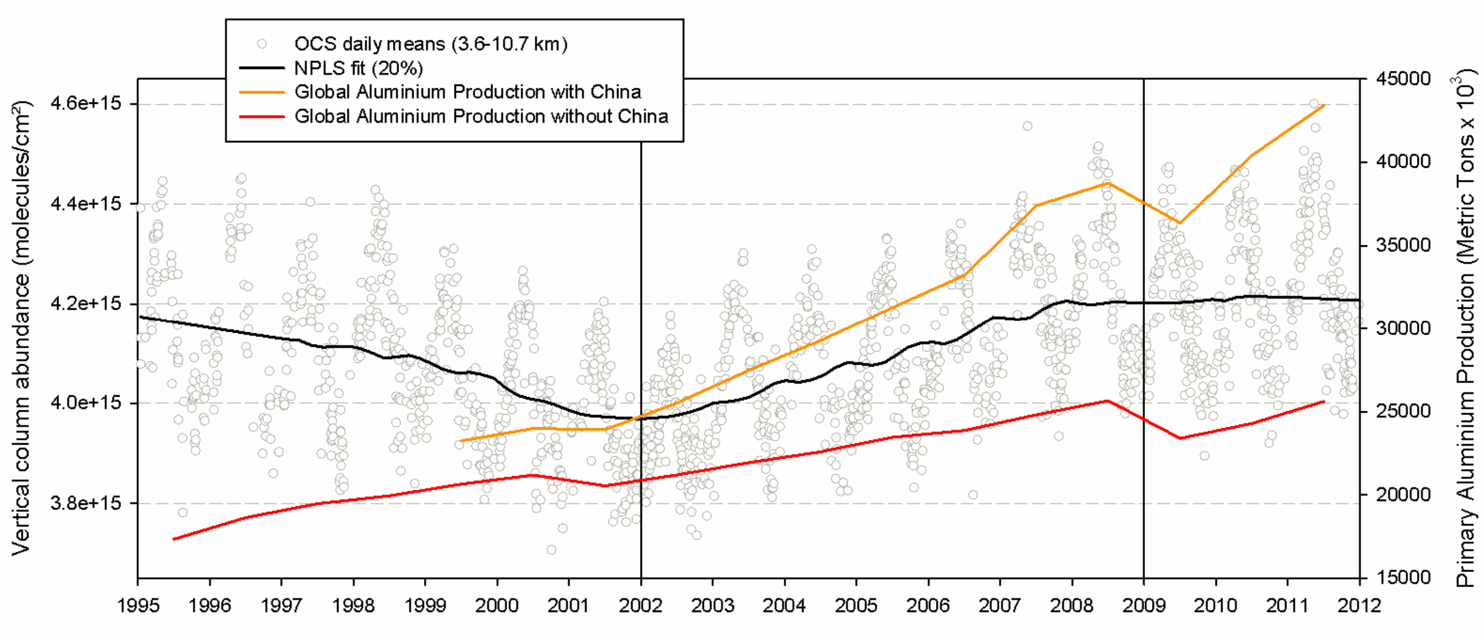
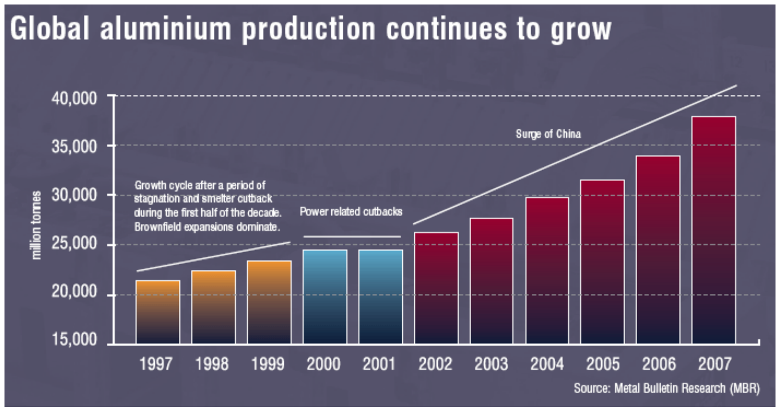


- OCS trend for 2002-2008 time period: + 1.08% / year → + 7.6%
- Aluminium production trend for 2002-2008 period: + 13 millions tons → + 4% of OCS global emissions

International Aluminium Institute

- Members (private company) of IAI represent 80% of global production;
- Data for China are coming from a governmental association (CNIA – China Nonferrous Metals Industry Association).



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DIRECT ANTHROPOGENIC EMISSIONS: COAL COMBUSTION

Process	Flux ($Tg\ a^{-1}$)	Comment ($Tg\ a^{-1}$)	Reference
Coal combustion	0.036 ± 0.011		Chin and Davis (1993)
Industrial S recovery	0.002 ± 0.0015		Chin and Davis (1993)
Cars	0.006 ± 0.004	Dependant on sulfur levels in fuels	Fried et al. (1992); Watts and Roberts (1999)
Aluminum production	0.08 ± 0.06	Increasing to 0.32 by 2030	Harnisch et al. (1992)
Total	0.124 ± 0.061		

Watts, 2000

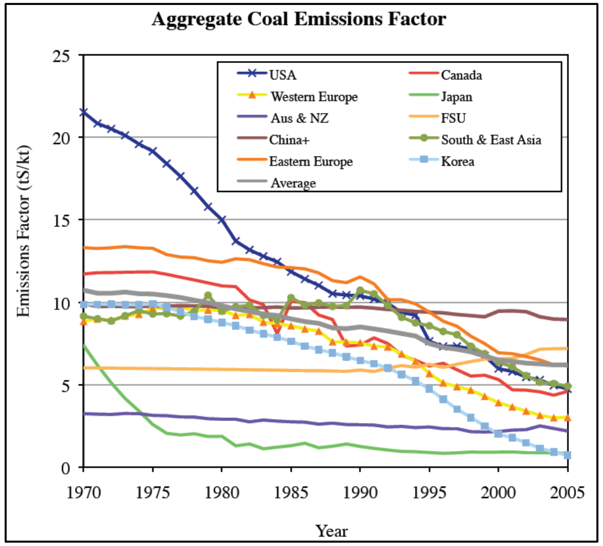
• World coal combustion has increased dramatically since 2002 and is mainly occuring in China;

• OCS emissions coming from coal combustion are very few documented: only one emission factor in the literature (OCS/CO_2 ratio of 2.3 10^{-6}) determined at the Cherokee Power Plant in Denver, Colorado (Khalil & Rasmussen, **1984**);

• Campaign of OCS observations over western Pacific (Blake et al., 2004) in 2001 shows pollution plumes origination from parts of China associated with high concentrations of OCS and high levels of coal burning;

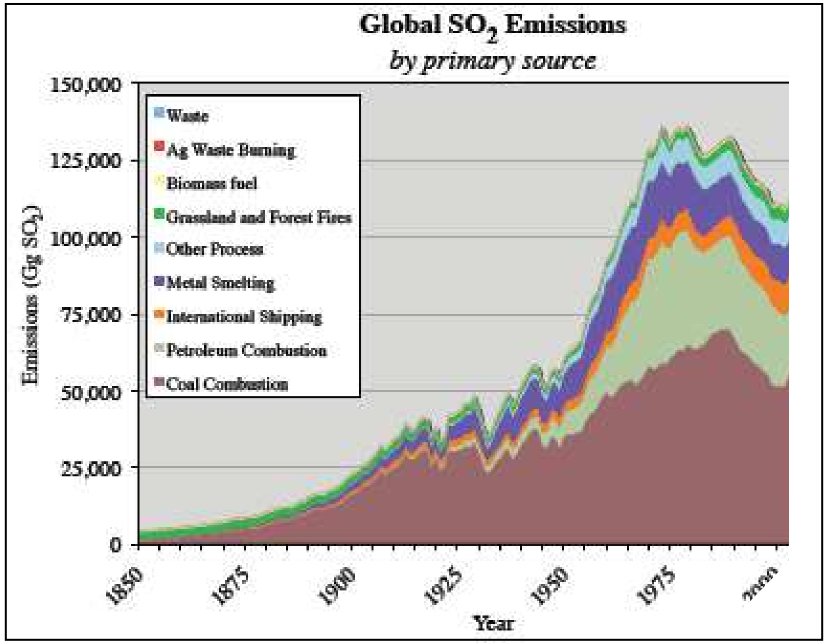
• Underestimation of Chinese emissions of OCS seems to be underestimated by about 30-100% due to uncertainties in OCS emissions from Chinese coal burning (Blake et al., 2004);

• Another campaign of OCS observations over Eastern USA and Canada in 2004 suggests that emission plumes coming from Ohia River valley seems to be cleaner (low-sulfur coal and modern coal-burning technology) (Blake et al., 2008).

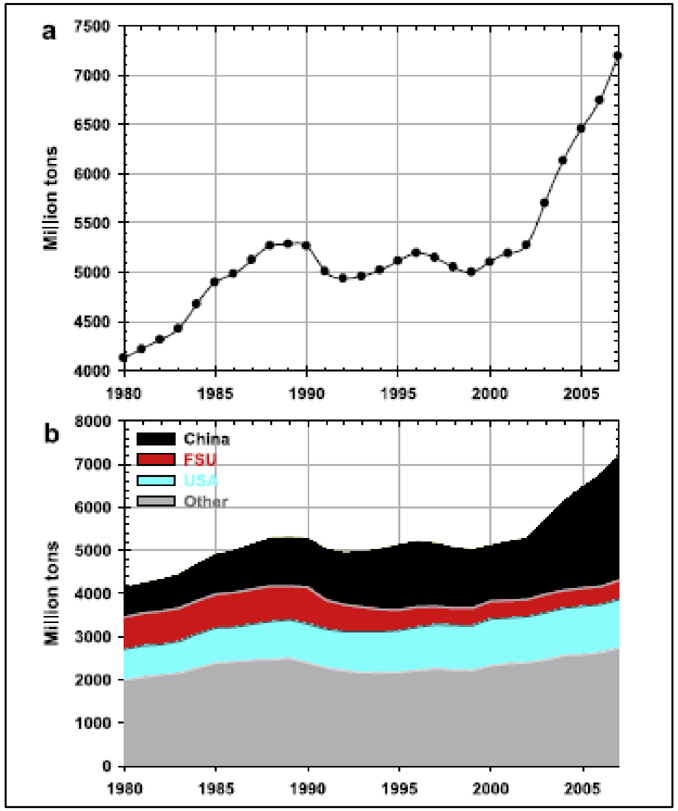


Smith et al., 2011

- Another way to estimate the evolution of OCS emissions coming from coal combustion: SO_2 emissions;
- Evolution of atmospheric OCS during the 20th century (increasing period followed by a decline during the past 20 years) coincide with evolution of anthropogenic sulfur emissions (Montzka et al., 2004);
- Recent estimation of global sulfur dioxide emissions shows a increase in recent years mainly driven by increasing coal combustion in China (Smith et al., 2011).



Smith et al., 2011



Hofmann et al., 2009

EDGAR EMISSION DATABASE FOR GLOBAL ATMOSPHERIC RESEARCH

in collaboration with Netherlands Environmental Assessment Agency ies JRC EUROPEAN COMMISSION

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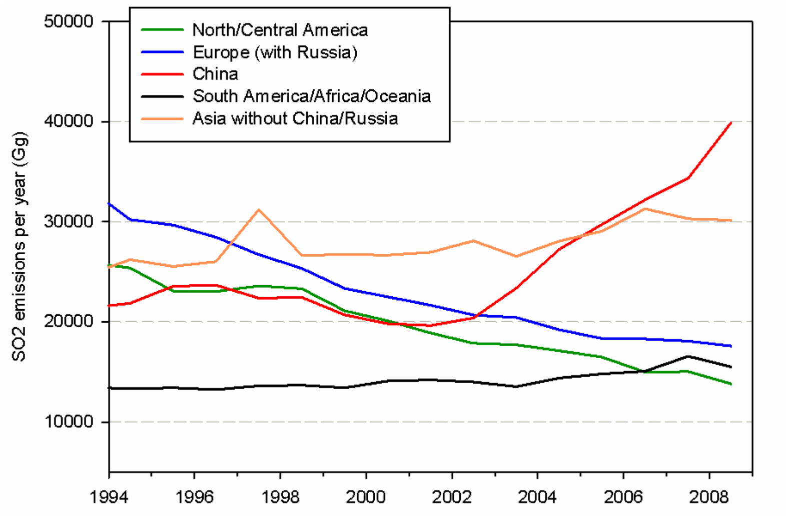
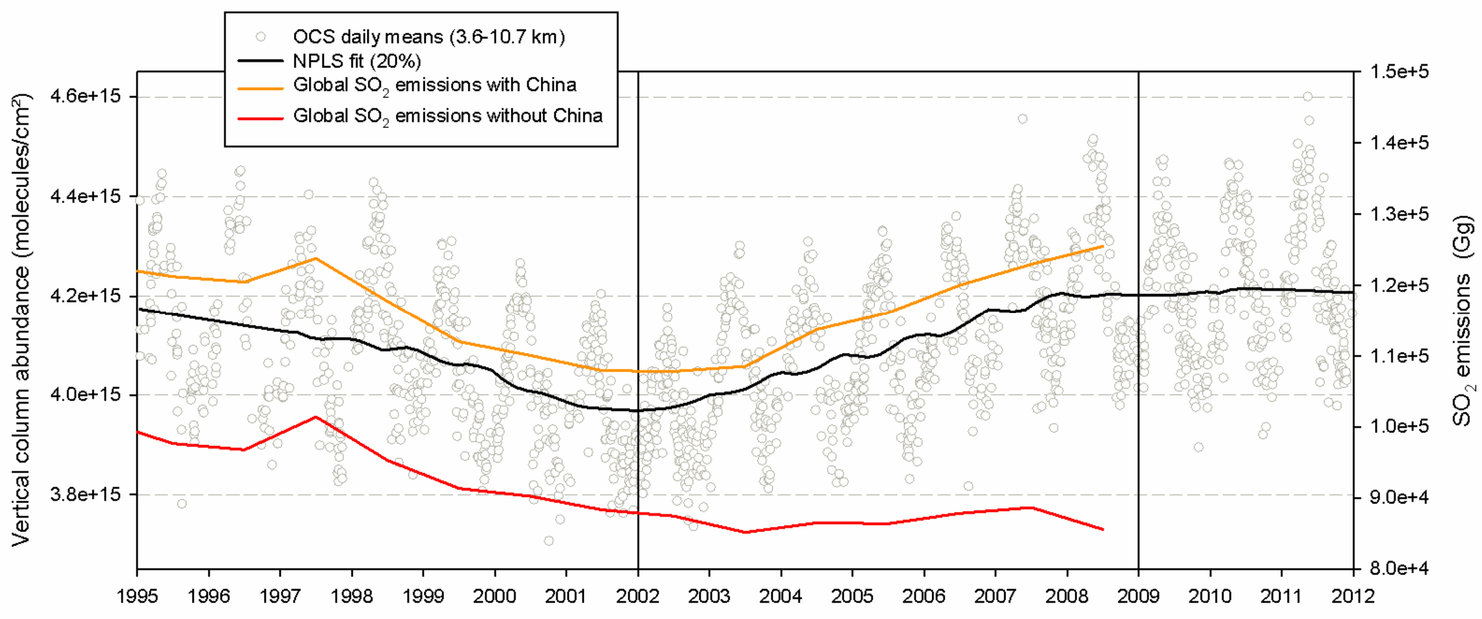


EDGAR v4.2 release

The new version v4.2 of the global EDGAR emissions inventory covers all greenhouse gases included in the Kyoto Protocol (i.e. carbon dioxide, methane, nitrous oxide and the fluorinated gases), ozone precursor gases, and acidifying air pollutants per source category at country level, and gridded with 0.1 deg by 0.1 deg resolution, for the time period from 1970 to 2008



- OCS
- FTIR
- Tropo
- Strato
- **Discussion**
- Conclusion

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CONCLUSION

• FTIR measurements at Jungfraujoch show the end of the decreasing period for TROPOSPHERIC OCS in 2002 with a new positive trend of more than 1% per year until 2008

• Increasing period in agreement with in situ measurements at a comparable site

• Anthropogenic emissions have the potential to be responsible of this, especially fast growing aluminium production and coal combustion in China

• No significant trend for STRATOSPHERIC OCS, both for FTIR measurements at Jungfraujoch and for ACE-FTS measurements in the 41.5-51.5°N latitudinal band

• As a consequence: OCS does not seem to bethe main contributor to SSA layer

THANK YOU FOR YOUR ATTENTION !