



Investigating source origins and photochemical processing of the VOCs during the MINOS-2001 campaign

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MAX-PLANCK-GESSELLSCHAFT

Volatile Organic Compounds

- Reactive compounds (hydrocarbons, oxygenated compounds...) → lead to the photochemical build up of tropospheric ozone (in high NO_x environments)
- Long lived compounds (organo-halogens, CFCs...) → their capacity to release chlorine or bromine in the stratosphere (leading to ozone destruction) has led to the phasing out of production of several halocarbons (Montreal Protocol and amendments).



Variability of hydrocarbons and halocarbons during MINOS

Variability concept

- Intuitively, the reactive, short-lived species are more variable than the long-lived ones.
- Jobson et al.¹ have derived the following empirical relation between variability and lifetime:

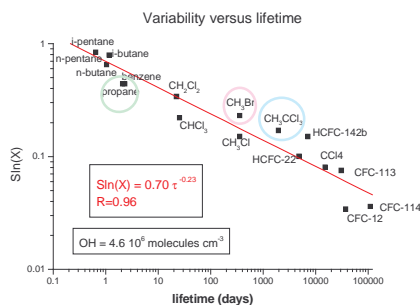
$$S_{ln(X)} = A \tau^b$$

(S: standard deviation, X: mixing ratio of the compound, τ : lifetime, A and b: two fitting parameters)

- b describes the importance of sink/source terms in the regional variability budget ($0 < b < 1$)

→ Remote places: strong dependence between variability and lifetime ($b \sim 0.5$)

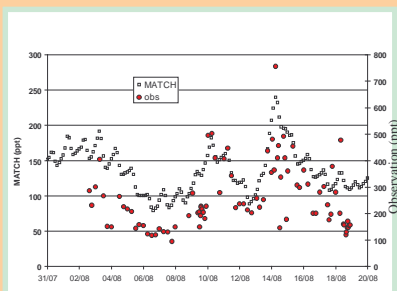
→ Other places: lower dependence between variability and lifetime due to the influence of local sources ($b \ll 0.5$)



Variability during MINOS

- The lifetime of the reactive compounds has been estimated by using an average OH value of $4.6 \cdot 10^6$ molecules cm⁻³ and by assuming that OH is the only sink of these compounds.
- A clear trend is observed: $S_{ln(X)} = 0.70 \tau^{-0.23}$ ($R=0.96$).
- The b coefficient of 0.23 reflects that the site of Finokalia represents some intermediate condition between remote sites³ and sites directly in the vicinity of sources⁴

Propane

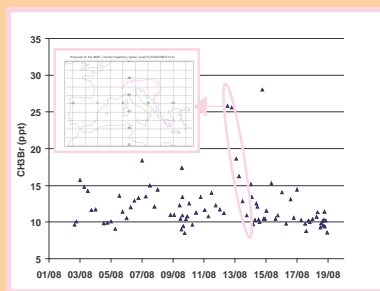


- Background level: ~ 120 ppt
- Observation of several pollution events due to the influence of various anthropogenic sources, mainly originating in Eastern Europe (fossil fuel combustion for the 3rd of August, biomass burning for the 10th August...)

Comparison with the MATCH model⁵

- The global model MATCH (Model of Atmospheric Transport and Chemistry -Max Planck Institute for Chemistry version) reproduces quite well the main features observed during the campaign, suggesting that the meteorology and the chemistry used in the model are realistic.
- However, the model underestimates the propane mixing ratios by a factor of 1.5 to 3, which is likely due to an underestimation of the propane emissions used in the model.

Methyl bromide



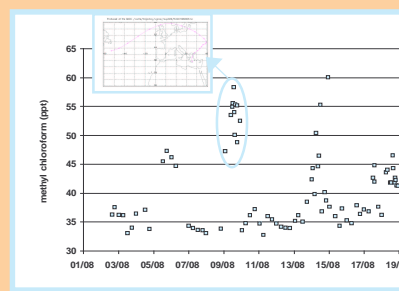
Methyl bromide (CH₃Br)

- Globally, mostly emitted by oceans but is also industrially produced and used for agricultural purposes (soil fumigation)
- Since 1995, its production in developed countries has been capped at 1991 levels and will be phased out in 2005

Methyl bromide during MINOS

- Background level: 12 ± 3 ppt
- Significant peak observed on the 12th of August corresponds to 10-days back trajectories originating from Western Europe
- Italy, the largest consumer of CH₃Br in Europe, could be the source of this event

Methyl chloroform



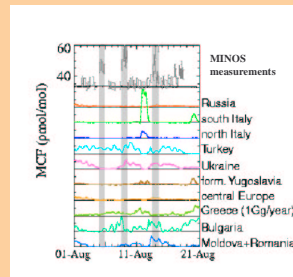
Methyl chloroform (CH₂Cl₂)

- Widely used over 40 years as a solvent
- Commonly used to estimate OH distribution and trend^{6,7} (OH being its unique tropospheric sink)
- Due to its ozone depleting capacity, its production has been phased out since 1996 in developed countries
- The assumption that CH₂Cl₂ emissions are now almost zero for the mid-latitude countries of the northern hemisphere is made in many studies⁷

Methyl chloroform during MINOS

- Background level ~ 35 ppt
- Several significant deviations from the background observed during the campaign
- Suggests the existence of on-going emissions of methyl chloroform
- Back-trajectories and model simulations (see below) suggest that these emissions come from Eastern Europe

Current OH determination and trends based on CH₂Cl₂ have to be revised⁸



The zoom version of the atmospheric-tracer transport model⁹ allows study of the European region with a horizontal resolution of 1° by 1°. The reference simulation of the model considers an emission of 1 Tg methyl chloroform for the whole Europe. Sensitivity simulations have been performed by considering an additional methyl chloroform source (equivalent to 10 Tg/year) for the different European countries which could have influenced observations in Crete.

Conclusions

- Propane variations during MINOS are dominated by the influence from anthropogenic sources originating in Eastern Europe. A comparison with the global model MATCH shows that the model reproduces quite well the general features of propane variations but underestimates significantly its mixing ratios (likely due to emissions underestimation).
- A significant peak of methyl bromide observed during MINOS likely reflects its large agricultural use as a soil fumigant in Italy.
- The MINOS experiment has confirmed that methyl chloroform is still emitted in some mid-latitude countries (despite the phase-out of its production). The large underestimation of its current emissions could lead to erroneous OH estimation (distribution and trends).

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