

***Interactive comment on “Origin of anthropogenic hydrocarbons and halocarbons measured in the summertime European outflow (on Crete in 2001)” by V. Gros et al.***

**V. Gros et al.**

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We would like to thank both reviewers for their constructive comments which have helped to improve the manuscript for ACP. Our detailed replies to these comments are given below.

Reviewer 1

‘Specific comments’

The information given by the reviewer on the variability concept has been incorporated in the revised manuscript.

‘The variability concept is based on the assumption that the chosen compounds have, more or less, the same source distribution. To a first approximation this is the case

Full Screen / Esc

Print Version

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Discussion Paper

for the compounds reported in this paper, which are mostly of anthropogenic origin. Methyl chloride (chloromethane) and methyl bromide (bromomethane) are exceptions, as they have a globally important oceanic source (Brasseur et al., 1999). However, we note that no clear evidence for an ocean source or sink for either gas could be derived from the variability analysis of samples collected in the southern Pacific marine boundary layer (Colman et al., 1998).'

Following the reviewer's comment, the discussion on the biomass burning episode and the corresponding methyl bromide has been improved:

'Secondly, although biomass burning has been estimated to contribute about 15% to the global budget of CH<sub>3</sub>Br (Lee-Taylor et al., 1998), no significant enhancement of this compound is observed during the polluted event of period 3 where biomass burning influences predominated. We note that considerable variability in the emission ratios of CH<sub>3</sub>Br from biomass burning processes has been observed, depending strongly on the bromine content of the fuel and on the proportion of flaming to smoldering combustion (Andreae and Merlet, 2001). However, even if we consider the upper limit of published CH<sub>3</sub>Br emission factors versus CO (Blake et al., 1996 and references therein), the 100 ppbv CO enhancement observed during this episode (Salisbury et al., 2003) would lead to a CH<sub>3</sub>Br enhancement of about 1 pptv. This value, which represents the maximum expected impact, is only slightly higher than our analytical precision, which would explain why there is no significant enhancement of methyl bromide during the biomass burning episode.'

'Technical comments' We have reworded the abstract according to the reviewer's suggestion. All the other technical comments have been taken into account. In particular we now use consistently the names 'methyl bromide' and 'methyl chloride'.

Reviewer 2

All the minor corrections suggested by reviewer 2 have been made and we detail below our answer to his/her specific comments.

Abstract Following the suggestion of reviewer 1, we have now reworded the abstract and explain the significance of the linear relationship.

We now use the names 'methyl bromide' and 'methyl chloride'.

## Introduction

We now refer to the studies performed at Mace Head: 'Several background studies have already reported the expected decrease of some of these compounds in the atmosphere and have also provided information about their regional sources. For instance, measurements of diverse halocarbons performed at Mace Head, Ireland, were used to estimate the intensity and distribution of their western European emissions (Ryan et al., 2001 and references therein). To our knowledge, no measurements have been performed directly in the outflow from eastern Europe in order to determine the eastern European contribution to their global budgets.'

## Section 2

### Section 2.1

As requested by the reviewer, we now give more details about the experimental procedure:

-about the Teflon membrane pump, the make and the origin are now given 'Using a Teflon membrane pump (KNF, Neuberger, Germany)'

-concerning the canisters: 'Air samples were pressurised in 2.4 L electropolished stainless steel canisters previously flushed with synthetic air and then pressurised to about 3 bar. Canisters were made at the workshop of the Max Planck Institute and were equipped with stainless steel valves (Nupro SS4H).' 'The canisters were not humidified but the quite high relative humidity observed during the MINOS campaign (63% on average) was considered to be sufficient to prevent losses associated with dry air.'

-about the working standard: The working standard is described at the beginning of

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Print Version

Interactive Discussion

Discussion Paper

section 2.3 and we now refer to this section when we first mention the use of the working standard. Additional information on the working standard stability has been added.

'Calibrations were performed against a working standard, a 10-L aluminium cylinder (Scott Marin, Riverside, California) filled at the Finokalia station two months before the campaign by using a three stage RIX oil-free piston compressor (Mak and Breninkmeijer, 1994). This cylinder, along with a second, filled a couple of hours later, was then calibrated at the National Center for Atmospheric Research (NCAR, Boulder, Colorado) relative to a gravimetrically prepared standard referenced to standards by the National Institute of Standards and Technology (NIST) (estimated accuracy of 2-3%). Therefore all the VOC measurements presented in this paper are calibrated on the NCAR calibration scale. Details of the NCAR calibration procedure are given in Schauffler et al. (2003) and references therein. About one year after the collection of these two cylinders, we measured our working standard against the other calibrated cylinder and we found the expected concentration (3.5 % difference on average). Assuming the two cylinders (which were taken at different times of day) did not drift in exactly the same way, we may conclude that the concentrations in our working standard did not drift over the period of MINOS measurements.'

-about the stability test in the 2 sub-samples: The two cylinders were measured against the working standard as now specified in the text.

## Section 2.2

-concerning the modification of the GC-MS: 'A sample preparation/cryoconcentrator unit was built (as detailed below) and the valves/heating system was automated using a custom built electronic programmable controller.'

-concerning the exact volume of sample determined: 'A known volume of sample (about 1 liter) was cryogenically concentrated at -72°C using a Neslab cc-100 circulation cooler (Portsmouth, USA) at a flowrate of 30-40 ml min<sup>-1</sup> in a stainless steel

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microtrap (length: 30 cm, ID: 0.076 cm), packed with porous silica beads (Unibeads 1S, 80/100 mesh, Alltech) over a length of about 10 cm. The exact volume sampled was determined by the pressure difference in a known volume downstream of the trap, held at 50°C.'

-concerning the agreement between two measurements of the same sample: 'More than half of the samples were measured twice and, on average, the two measurements agreed within 3.5% (standard deviation over mean).'

### Section 2.3

-concerning the treatment applied to the aluminium cylinder In this case the word 'treated' has been mistakenly inserted and has been now removed. The aluminium cylinder was simply compressed with Finokalia air without pre-treatment.

-concerning the NCAR calibration It is now clearly stated that our measurements are calibrated on the NCAR calibration scale and a reference to the NCAR calibration procedure is given (see above our answer concerning the working standard).

-concerning the frequency of the calibration: We agree with the reviewer that a more frequent calibration would have been more appropriate. We ascertained this during the analysis and we have now adjusted this procedure accordingly, performing at least two calibrations a day.

-concerning the linear decrease of the MS sensibility It is now mentioned in the text that the almost linear decrease of the MS sensibility was concluded after that the calibration was performed in the middle of the week. 'A calibration was once performed in the middle of the week and it was found that the decrease of MS sensitivity over the week was almost linear'

-concerning the blank 'At least two blanks (using the same analytical procedure but without collecting sample) were performed at the start of each measurement sequence'

-concerning the linearity: 'Linearity of the analytical system was better than 3% for all

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the compounds presented. The linearity was determined by injecting different amounts (from 0.03 L to 1 L) of the same sample and by monitoring the corresponding peak area. The obtained linear fits were used to calculate the residuals. The residuals were calculated as the difference between the actual value and the linear fit (for each point between 0.03 and 1 l injections), these differences being then divided by the actual volume that was injected and finally multiplied by 100. The average of these residual values gave the linearity in percentage terms of individual data points for each specific compound.'

-concerning the analytical precision: 'Analytical precision of 10 consecutive analyses of the same standard was better than 5 % for all compounds except for methyl bromide (7%) and methyl chloroform (7%). We note that these relatively high values for methyl bromide and methyl chloroform are due to outliers. When omitting the extreme values (the lowest one and the highest one), then the precision is also better than 5% for these two compounds.'

## Results and discussion

We have now added a paragraph to compare the MINOS measurements with other measurements performed in the northern hemisphere.

'For the most reactive compounds, i.e. the hydrocarbons, a comparison with other measurements in the northern hemisphere is not straightforward as their concentrations are very variable depending on the proximity to, and intensity of their sources. Their variability in terms of sources and photochemical processing during MINOS are described in detail in section 3.2. For the long-lived compounds, the most extensive set of measurements is from the ALE/GAGE/AGAGE network (Prinn et al., 2000), which consists of 5 measurement stations in the northern hemisphere and 2 stations in the southern hemisphere. We compare our data to the measurements performed at Mace Head, the only ALE/GAGE/AGAGE station located in Europe. Five long-lived compounds (CFC-12, CFC-113, HCFC-142b, CHCl<sub>3</sub> and CCl<sub>4</sub>) were measured both at

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Mace Head and at Finokalia during August 2001. The corresponding monthly means are reported in Table 1 for Mace Head and show a good agreement with the MINOS data. The highest difference is observed for CFC-12 between the MINOS selected clean air data and the Mace Head data. However, the campaign average agrees with the Mace Head August average within the uncertainty range.'

#### Section 3.2.2.

Concerning possible co-elutions with propane: The propane peak is identified by both retention time and qualifying ions. There are relatively few possible VOC isomers in this high volatile region of the chromatogram. The only proximate peak is that of propene which is nevertheless always well separated from propane under these conditions. No overlapping peak was seen. In addition, the propane identification was confirmed using mass-scan in combination with the NIST reference library. To answer the reviewer's request, we have added the monitored ions for each compound shown in Table 1.

Section 3.2.4 As the speciation of the VOCs was not available for the new version v3.0, the version 2.0 of EDGAR was used. The calculation presented in section 3.2.4 shows that the ratios at the emission point are consistent with those measured at Finokalia. This suggests that the speciation used in the database is correct and therefore that the magnitude of total VOC emission is in error.

It is now specified that the emissions were taken from EDGARv2.0.

Section 3.3 According to official production statistics as gathered by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS, 2003) and the emission estimation methodology as applied by Fisher and Midgley (1993) the release of CFC-113 to the atmosphere has decreased from 100,000 metric tons in the 1980's to 2,500 metric tons in the year 2001. This implies that the emissions of CFC-113 are not significant globally.

Following the suggestion of the reviewer, the following sentence has been added at the

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end of section 3.3 'It is important to note that these emissions (MCF and CFC-113) are still relatively small and that they will not have a significant adverse effect on the predicted recovery of stratospheric ozone.'

#### Section 3.4

The interpretation of the methyl bromide peak we give here is the most probable, as methyl bromide is used intensively (as soil fumigant) in Italy, which the back-trajectories showed to have influenced the MINOS observations at exactly the time of the observed methyl bromide peak. However, we can not completely rule out the contribution of another source and this is now mentioned in the paper.

It is very unlikely that the variability observed arise from the use of canisters. Although no other systematic test about the stability of compounds in canisters has been performed, a number of canisters similar to those used in MINOS have been measured twice with a delay of several months (4-6 months) and they did not show any significant change in the methyl bromide concentrations. In addition, the peak of methyl bromide observed during MINOS not only shows two values higher than 25 pptv but also a progressive decrease of the concentrations of the next two samples to background levels, which is consistent with atmospheric variability.

According to the sensitivity study (figure 4), air measured on the 14th August was mainly influenced by eastern Europe. However, as this is a lone high value, it is not emphasised in the paper.

The caption to Table 1 has been changed according to the reviewer's suggestion.

The discussion on the biomass burning episode and the corresponding methyl bromide has been changed according to comment of reviewer 1.

We now refer the reader to the companion paper of Salisbury et al. (ACP, 3, 925-940, 2003) for a map of the region and the complete description of air mass origin observed during the MINOS campaign.

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References AFEAS, Alternative Fluorocarbons Environmental Acceptability Study, [http://www.afeas.org/prodsales\\_download.html](http://www.afeas.org/prodsales_download.html), 2003 D.A. Fisher and P.M. Midgley. "The Production and Release to the Atmosphere of CFCs 113, 114 & 115," Atmos. Environ., 27A, 271-276, 1993.

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Interactive comment on Atmos. Chem. Phys. Discuss., 3, 1893, 2003.

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