

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

**Anonymous Referee #2**

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The paper describes measurements of a suite of hydrocarbons and halocarbons made on Crete during the MINOS experiment in the summer of 2001. The measurements are used to investigate the origin of the different air masses sampled during the campaign and, in the case of propane, to assess the quality of regional emission inventories. Perhaps the most significant finding is the evidence for continuing emissions of methyl chloroform from parts of Eastern Europe which may have important consequences for the calculation of global OH trends.

The paper is interesting to read and is generally well written and presented. However, there are a number of points that need to be addressed before publication in ACPD. These are outlined below.

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## Abstract

Lines 5-6: "we found the compounds describe a linear relationship." The authors should explain why this is significant.

Page 2, line 1 (and elsewhere): bromomethane is normally referred to as methyl bromide.

## Introduction

Page 2, line 18: This is a minor point, but the Montreal Protocol actually limits consumption of CFCs not simply production, where consumption = (production + imports) - exports.

Page 2, line 19-20: change to "Several background studies ..... decrease of some of these compounds...."

Page 2, line 20-22: European emissions of some halocarbons have been estimated previously from measurements at Mace Head, Ireland (e.g. Ryall et al., Atmos. Env., 35, 2507-2523, 2000; Simmonds et al., Atmos. Env., 30, 4041-4063, 1996) . These should be referenced here.

## Section 2. Experimental

I believe this is the first time that this analytical system has been described in the open literature so I would like to see more details about the experimental procedures and calibration. Some suggestions follow:

### Section 2.1

What was the make of the teflon membrane pump?

Who was the manufacturer of the canisters? Were the canisters humidified before use?

Page 3, line 12: should presumably read "...high pressure working standard...." ? What was the working standard and how do we know that the concentrations in this did not

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drift over the 6 month period of measurements?

How was drift in the 2 sub-samples monitored? Were they analysed against a primary standard (if so, what was it?) or just against each other ?

Page 3, line 15: should read "The exception was chloroform which showed ...".

Page 3, line 17: "In August the site is ..." Should this be is or was ?

## Section 2.2

In what way was the GC-MS modified? (bottom of page 3)

How was the exact volume of sample determined?

Page 4, line 16: " the two measurements agreed within 3.5%". Does this mean  $\pm 1\sigma$  standard deviation?

## Section 2.3

What was the treatment applied to the aluminium cylinder?

Was the primary standard at NCAR calibrated for all the compounds in Table 1 ? Do NIST provide calibrated standards for the halocarbons as well as hydrocarbons? Perhaps a reference to the NCAR calibration procedure could be given here. Can the authors state that their measurements are calibrated on the NCAR calibration scale? It is often helpful to be able to trace measurements back, where possible, to well defined/published calibration scales.

In order to improve the precision of the measurements it would have been much better to have analysed the working standard at a much higher frequency and then extrapolated over shorter time periods. Was there a reason why the working standard was analysed so infrequently? How do the authors know the "decrease of MS sensitivity over the week was almost linear" when calibrations were only performed at the beginning and end of the week?

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What was the composition of the blank sample (page 5, paragraph 2)?

How was the linearity of the analytical system determined (page 5, paragraph 3)?

The analytical precision for methyl bromide and methyl chloroform seem rather high (7%). Can the authors account for this?

### Results and Discussion

With the exception of a short paragraph on page 13, there is little comparison of the MINOS data with other reported measurements. Although a full review is not necessary here, some indication of previous studies would be useful. How do the mixing ratios shown in Table 1 compare with other NH measurements? This should be relatively straightforward for the longer-lived halocarbons and would help the reader assess the quality of the MINOS measurements.

Page 7, line 13 and 23; should read "back-trajectory analysis" and "back-trajectory calculations"

Page 7, line 22: specify "BC" as black carbon.

### Section 3.2.2

On page 9 the authors rule out measurement error as a source of the high measured propane mixing ratios. However, can they also rule out the presence of co-eluting compounds in their GC analysis. It would be helpful to know which ions were monitored for propane (and indeed the other compounds listed in Table 1) and whether any tests have been performed to confirm there are no co-elutions.

Page 9, line 14: replace "as well" with "either", i.e. "... cause the difference either: ..."

Page 9, line 15: add "the", i.e. "... not responsible for the discrepancy ..."

### Section 3.2.3

Page 11, line 25: add a comma after v3.2

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### Section 3.2.4

Having convinced the reader in the previous section that there are significant likely errors in V2.0 of the EDGAR database, is it valid to now use the same database for the calculations presented in section 3.2.4 and Table 3? Are the ratios at the emission point likely to be in error or is it just the magnitude of the total VOC emission?

Page 12, line 15 (and Table 3): specify which EDGAR database the emissions were taken from.

Page 12, line 21: should read "4.0 x 10<sup>6</sup> molecules ..."

### Section 3.3

The evidence for continuing emissions of methyl chloroform is very significant for determining the global OH trend as the authors correctly point out. However, to avoid possible confusion, it could also be stated that the emissions are relatively small and will not have an adverse effect on the predicted recovery of stratospheric ozone. Are the emissions of CFC-113 significant globally ?

Page 14, line 4: replace "would have" with "had"

Page 14, line 5: delete "it", i.e. "... as was clearly..."

Page 15, line 3: "can not" should be one word "cannot".

Page 15, line 6: add "... determine the global mean ...."

Figure 4: What is the y-axis scale for the individual coloured time series? The reference simulation is presumably the black line running through the lowermost observations?

### Section 3.4

Methyl bromide also has a number of other proposed terrestrial/coastal sources (salt marshes, wetlands, etc - see, for example, WMO Scientific Assessment of Stratospheric Ozone 2002). Could any of these account for some of the variability in the

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MB data? Alternatively, is it possible that much of the variability could simply arise from the use of canisters? Storing compounds like MB in canisters for up to 6 months is not ideal, particularly if the canisters have not been prepared correctly. Have the authors carried out any storage tests other than the 2 canister test described in section 2.1?

What is the likely origin of the high value seen on August 14 ?

In Table 2, the clean air MB average is stated as 15 ppt. Comparing this with Figure 5, period 2, this seems a little high and is probably biased by the one high value seen on August 7. A typical NH clean air background should be in the range 9-11 ppt. Perhaps the authors should state in the caption to Table 1 that the clean air concentrations are an average of x samples collected on August 7.

Page 16, line 8-9: What is the significance of the CO measurement? Is MB more likely to be emitted in the flaming stage than the smoldering phase?

Summary and conclusions

Page 16, line 24: "VOC" should be "VOCs".

Page 17, line 7: add "...models are to be usefully compared with measurements".

Page 17, line 10: replace "completing" with "complementing".

References

Bottom of page 20, Prinn (2001) - need to include the rest of the authors. All references to Prinn (2001) in the text should be changed to Prinn et al. (2001).

General point

A map of the region would help when looking at the likely origin of the pollution episodes discussed.

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