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Interactive comment on "Estimates of European emissions of methyl chloroform using a Bayesian inversion method" *by* M. Maione et al.

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Responses to Referee 2

p.8215, line 23. Since there is some detail given about the analytical procedure, I was curious about the statement about the standard humidification and linearity. Multi-level calibration and linearity are not discussed in the method description. How is this done and how often is linearity checked? Is there an issue with non-linearity in the measurement of the higher level signals? Also, it's not clear to me how a uniformly humidified standard ensures "a close similarity in composition" to air at a coastal station and also a mountain site. Probably not a big deal, but if not then just leave out all the boiler plate that is not supported nor particularly relevant to the current manuscript.

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Reply: Multilevel calibration and linearity tests are a hard to solve but strictly needed issue for any analytical method. There are several source of possible non-linearity of the whole method that could lead to a deviation of the ideal constant sensitivity of the detector towards the varying concentrations. A brief but exhaustive description is reported by Miller (Miller et al., 2008) and can be extended to our analytical instrument. It's not an easy / feasible task to prepare a multi-level calibration curve due to the costs and intensive labour involved in preparing and maintaining a set of multi-level mixtures. A workaround is to test the system by the same mixture but with increasing the sample volume. This test has a limited concentration range verification, but give enough information on the system behaviour and performances. Also the use of real air mixture as a working standard for the systematic calibration and for tests limits the overall bias of the method. For that reasons, the whole system was tested (by the increasing sample volume technique) on the lab prior setting it on the field and is regularly checked every time a sensible part is changed for some reason, such as every time the adsorbing trap is replaced (to verify the breakthrough volume and the recovery/desorbtion efficiency of the new trap), or the MS is opened for the service (change of the electromultiplier horn), or when a new quaternary/working standard tank is installed (for which there is a composition change from the old one). Methylchloroform, fortunately doesn't show any linearity issue to solve -at least within the limit of the test capability described above-; that kind of problems are most likely affecting very low boiling point compounds, for which the system has been anyway optimized, that are analysed at the station with the same instrument. By the way, as a general agreement, the arising non linearity, in case of large mole fraction samples, are accounted for by an increase of the associated uncertainty, since it is calculated as constant percentage of the absolute concentration.

Also, it's not clear to me how a uniformly humidified standard ensures “a close similarity in composition” to air at a coastal station and also a mountain site.

Reply: A partial response to this comment is contained in the above reply: humidification reduces uncertainties and non-linearity effects of the analytical method (the

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whole system is tested and calibrated with real air mixtures). Furthermore, it has been demonstrated that the humidification procedure of the air during the pumping of standard tanks ensures the stability of the compounds avoiding or minimising the degradation on the pump surfaces and on the surface of the cylinders.

p.8220, line 1. The baseline attribution seems reasonable to me, but I wonder if there are any comments about the baseline irregularities, such as the concentration dip at CMN in Jan 2006, or the longer term cycle at MHD throughout 2002-2003.

Reply: The irregularities in the baseline can be ascribed to the interaction with the OH, whose concentration is not constant in different years and seasons, as well as by changes in global emissions at a temporal scale shorter than a year.

p. 8220, line 19. Obviously it is not just the location of the MCF source nearer to CMN, but also the wind direction and transport.

Reply: yes, we agree with this comment and we modified the sentence accordingly.

p. 8217, line 25. Please add “emission estimate” or similar after “a priori”. Try to avoid modelling jargon.

Reply: we modified the text accordingly.

p. 8223, section 3.2.3. I was struck by the distinction of the influence of SEF on the observed mixing ratios. Visually, all of the excursions, with the exception of a period in early 2009 at CMN, are due to the influence of SEF. This would seem to indicate that all of the other information on other emission sources are contained in mixing ratio excursions above background that are in the 0.1 – 0.3 pptv range, which is close to the uncertainties in the background itself. Is this true? It seems remarkable to me. Can this aspect be discussed a bit further?

Reply: The plot in Figure 6 is obtained applying an on-off filter, i.e. it shows when an air mass that reaches the receptor site has first passed over the SEF region (red points). This plot shows how nearly all the most intense enhancements are associated to a contribution from SEF, but this does not mean that all the enhancement is due to a contribution from the SEF region. In other words, any single enhancement could in principle contain also contributions from other regions, but has anyway passed through the SEF region. Anyway, the referee correctly points out how the contributions from other sources are very small at the receptors, being the other sources weaker by order of magnitudes than the SEF and, in the case of CMN and JFJ, further or less upstream than SEF.

p. 8221, line 1. It is noted that the MCF emissions to soil and water are not included in the a priori emission estimates (though it is suggested that these sources are revealed in the analysis). It would be useful to understand the relative magnitude of these sources, since I assume they are just a slower release to the atmosphere compared to direct emission.

Reply: we do not have enough information to quantify the emissions to the atmosphere deriving from the release of MCF to soil or water. The E-PRTR inventory does not provide information on the amount of the released MCF. Furthermore, these sources are too small and remote from the stations to be quantified through the model. Therefore, even if this is an interesting topic, we cannot examine it in depth in this study.

p. 8221, Figure 4. Though I could see the location of the sites on other Figures, the black dots that designate the measurement sites tend to disappear in the dark purple.

Reply: yes, we agree with this comment and we modified the black dots accordingly.

General comment: The appendices provided little information that I thought was particularly important for the analyses. I would expect that the basic findings of the Appendices could be incorporated into the main text and reduce the overall length of the manuscript. Some parts of the appendix discussion, too, e.g. A1.4/Table A.2, were rather opaque and unintelligible to someone (me) with no expertise in evaluating model statistical tests.

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Reply: we would prefer to leave these contents in the Appendices in order to make the main text more concise. However, in order to improve clarity, we made substantial changes in the Appendices (See replies to comments from Referee 1).

General comment 2: It would interest me to know what other of the suite of trace gases measured at CMN (especially) can also be traced back to the SEF sources?

Reply: we didn’t find any significant correlation with any of the other compounds that are measured at CMN. Furthermore, most of the compounds monitored at CMN are still in use and, as a consequence, they have more distributed sources across the domain.

General comment 3: The emission estimates should be reported with some clear statement of the associated error. If stated in the text, I missed it.

Reply: we included in the text a reference to the Appendix where the associated errors are described in detail.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 8209, 2014.