

Interactive comment on “Formaldehyde (HCHO) in air, snow and interstitial air at Concordia (East Antarctic plateau) in summer” by S. Preunkert et al.

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Response to referee comments:

Anonymous Referee #1

Reviewer general comment: This paper reports first combined formaldehyde measurements in the air, snow and interstitial air in Antarctica. Formaldehyde is a key compound in atmospheric chemistry which can play an important role in the HO_x budget and therefore it is important to characterize its sources and sinks. This manuscript brings an interesting and original dataset which is thoroughly analyzed through differ-

C13149

ent aspects. Especially the formaldehyde budget is examined and confirms that snow is a net source of formaldehyde at the studied site but simulations with a model allow the authors to conclude that the gas-phase oxidation of methane remains the dominating source. Generally the paper is clear and well written. Nevertheless, there are some sections which could be improved to help the readiness of the paper (in terms of structure). Therefore I would recommend publication of this paper in ACP once the comments below have been addressed (Please note that my field of expertise covers only partly the results presented here).

Specific comments: Reviewer comment: The abstract should give the main conclusions (main results) of the paper and therefore should answer the objectives which are described at the end of the introduction. It is therefore recommended to include the important result about snow versus photochemical production contributions to the atmospheric formaldehyde in the abstract.

Authors response: Following the reviewer comment, we added the following at the end of the abstract: “Simulations indicate that the gas-phase production from CH₄ oxidation largely contributes (66%) to the observed HCHO mixing ratios. In addition, HCHO snow emissions account for ~ 30 % at night and ~ 10 % at noon to the observed HCHO levels”

Reviewer comment: The introduction could be a bit extended to give some more information about formaldehyde. Even if the authors have already addressed the question of formaldehyde in remote areas in previous papers; a few more information is needed for the readers who do not know these previous works. A short paragraph introducing formaldehyde in general (its main sources and sinks, its lifetime) and its role in atmospheric chemistry and especially in remote atmosphere would allow to have a broader view on the importance of this compound and would better introduce the objectives of this paper.

Authors response: Following the reviewer comment, we changed the introduction by

C13150

starting with an overall statement on HCHO as follows: “Over continents, formaldehyde is produced within the atmosphere during the oxidation of numerous hydrocarbons emitted by anthropogenic and natural sources and also directly emitted by combustion. In the remote marine troposphere, HCHO is thought to be mainly produced by the photo-oxidation of CH₄, the most abundant atmospheric hydrocarbon (Lowe and Schmidt, 1983). In addition to wet and dry deposition, the main sinks of HCHO are photolysis and reaction with OH leading to a typical HCHO atmospheric lifetime of a few hours (Seinfeld and Pandis, 2006). At remote high-latitude sites several studies were conducted over the Arctic and Antarctic snowpack to evaluate the importance of the snowpack as a formaldehyde source for the atmospheric polar boundary layer (Sumner and Shepson, 1999; Yang et al., 2002; Jacobi et al., 2002; Hutterli et al., 2004; Riedel et al., 1999; Salmon et al., 2008). The understanding of the budget of HCHO in polar region is of importance since HCHO represents an important source of RO₂ radicals in the remote polar atmosphere, and is therefore intimately linked to the oxidative capacity of the atmosphere in these regions. This is true in margin regions of Antarctica.”

Reviewer comment: It is suggested to introduce the “method and field campaign” section with a paragraph to present the overall experimental strategy (explaining that 2 campaigns were performed and how they complement each other).

Authors response: We agree that it is better to introduce the two field campaigns in an introduction paragraph. We added the following paragraph: Data presented in this study were obtained during two summer field campaigns having taken place at Concordia located on the high East Antarctic plateau (75°06’S, 123°33’E). The 2011/12 campaign conducted from late November 2011 to mid-January 2012 (i.e., the second OPALE field campaign) was mainly dedicated to document HCHO levels at two different heights in the air above the snow surface and to do a few HCHO measurements in interstitial air and in snow. During the 2012/13 campaign (December 22nd 2012 to January 25th 2013) HCHO was measured at different heights in air and firn in the

C13151

framework of the snow tower experiment SUNITEDC (Evolution du Sulfate et du Nitrate de l’air et de la neige de Dôme C). Hereby the priority was to gain a detailed picture of the HCHO distribution in the interstitial air of the snowpack. In the following section we first describe the analytical method used to measure HCHO. Then, for each campaign we present on site measurement set up and applied working conditions, as well as achieved detection limits in air, interstitial air and snow (Sect. 2.2 and 2.3). Finally, the model used to discuss the different source contributions to the atmospheric HCHO budget at Concordia are briefly introduced in Sect. 2.4.

Reviewer comment: The 2011/2012 field experiment (P32031, L23): could you give the standard deviation

Author response: The standard deviation is reported now: “Comparison of the two 15 m long airlines made by putting their air entries at the same height (1 m) showed no systematic differences (mean difference of 2.5 ± 40 pptv over 10 h). “

Reviewer comment: associated to the mean difference? (P32033, L13): “the contamination of firn air became weaker”: would it be possible to quantify this contamination and to show that it did not affect the presented results?

Author response: We added the absolute value of firn air measured at the end of the experiment, and we can argue that this value is in good agreement with the firn air measurements realized in 2012/13. The text was revised as following: “At the end of the season, the contamination of firn air became quasi insignificant as suggested by the observed HCHO values at that time (400 pptv at a depth of 10 cm) that are far lower than those observed at the beginning of the campaign and are in good agreement with those obtained during the 2012/13 campaign. Thus, it was possible. . .”

Reviewer comment: (P32038 L20): The daily cycle mentioned from 14 to 18 December is not clear for me (for example data at midnight have the same value than at 12h). Section 6 mentions an amplitude of 45 pptv but this is only valid for the period 19-28 December. Could this be discussed more detailed?

C13152

Author response: Thanks for this comment, you are absolutely right and we reworded this paragraph as following: "From December 14th to 18th, only a small day/night difference of HCHO values can be observed with slightly lower daytime values (116 pptv between 8:00 LT and 14:00 LT) than nighttime values (126 pptv between 15:00 LT and 7:00 LT). During the following period (December 19th to 28th) when air temperatures were enhanced, a marked daily cycle (amplitude close to 30 pptv) characterized by a broad minimum from 7:00 LT to 15:00 LT and a broad maximum from 16:00 LT to 6:00 LT is observed." In section 6 we also now specify "As mentioned in Sect. 3 (see also Fig. 9a) the diurnal HCHO cycle observed over the period from 19th to 28th December 2011 is characterized by a daytime minimum with amplitude reaching 30 pptv."

Reviewer comment: As the paper is currently pretty long, I'm wondering if it could be a bit shortened and more focused on its main objectives (sources and sinks of HCHO in Concordia, section 6). For this, some intermediate results could be presented in the supplementary material and only their main outcome would be presented in the main text. Two sections who could potentially be moved to the supplementary material would be sections 4.3.1 (just mentioning the main conclusion that the "polar snow appears often under-saturated with a particularly large depletion at Concordia") and section 5.2 (giving only the results from this other approach to calculate fluxes and all details being shifted to the supplementary material).

Author response: We feel that parts of paper that can usually be put as supplementary material are details on well-known approaches or data. This is neither the case for section 4.3.1 nor for section 5.2.

Concerning section 4.3.1, over the last 20 years, several studies aimed to investigate the physical processes driving the air/snow partitioning of HCHO. This is indeed a key point for which knowledge is mandatory to parameterize HCHO air/snow exchanges in atmospheric chemistry model simulations. Until now two laboratory studies were performed on ice (Burkhart et al., 2002, Barret et al., 2011) in which it was revealed that the thermodynamic equilibrium is the driving process of the air/ice partitioning.

C13153

However a direct comparison between these laboratory data and relationship between air and snow observed in the nature was before this present study limited to snow-pit in Greenland and in the snowpack in Alaska (here the comparison between ice and air having been done using ambient air concentration since no interstitial air measurements were available). The data set gained in our study allows to complete these sparse comparisons with Antarctic data (not yet available) to draw a more representative picture of the real HCHO firn/air equilibrium encountered in polar snow. The fact that laboratory air-ice studies and relationship observed at polar sites do not agree is a very important result, and shows that the ice/air equilibrium parameters derived from laboratory studies cannot be applied for real polar conditions. Therefore we think this paragraph brings new insights on this topic and has to remain in the main manuscript.

In Section 5.2 HCHO snow fluxes are calculated on the basis of gradients between firn-air and atmosphere. On a first sight this might be redundant to the HCHO flux calculations made on the basis of atmospheric gradients in section 5.1. However as detailed in section 5.1, the calculations made on the basis of atmospheric HCHO gradients between 1 cm and 1 m are very low and relatively inaccurate. Therefore it is very important to use an alternative method independent to the commonly used flux calculation done in section 5.1. In contrary to former studies in which only a few firn air data points were available, our data set allows indeed for the first time to do a reliable estimation of the snow air HCHO flux on the basis of atmospheric and firn-air HCHO data. The fact that HCHO fluxes calculated with both methods are in agreement strengthened the reliability of the HCHO flux estimation, what is important since this parameter has an important influence on the HCHO budget discussed in section 6. Given the innovative character of such a comparison we feel that it is legitimate to keep this paragraph in the main manuscript.

Reviewer comment: If other sections are shortened, the discussion on the results from the main section (6) could then be slightly extended. Section 6.2 could compare these results with other diurnal cycles of formaldehyde observed in Antarctica (and com-

C13154

ments on similarities/differences).

Author response: HCHO data obtained in Antarctica are available from the South Pole where no daily cycle is expected in relation to unchanged solar radiations over the course of the day, and at coastal sites. At the coastal site of Dumont d'Urville, Preunkert et al., 2013 detected a daily HCHO cycle with a maximum in the afternoon. As discussed by the authors of this previous paper, the shape of the daily HCHO cycle is a result of the interplay between the daily cycles of the different HCHO sources and sinks. However these daily variations of OH mixing ratios, photolytic rates, snow HCHO emission advected at the site (there is no snowpack at the immediate vicinity of the site) and HCHO deposition are again dependent on the daily variation of other parameter including boundary layer height, which are very site specific. Preunkert et al., 2013 made a sensitivity study in which parameters were adapted to achieve in simulations the observed shape of the daily HCHO course at DDU. Hereby it became obvious that only little changes of the daily course of input parameter can already change the daily course of HCHO. In view of that, we feel that a discussion on differences on diurnal cycle of HCHO between coastal and inland sites is quite complicated and not directly useful for this paper focused on the inland site of Dome Concordia.

Reviewer comment: The simulations were performed on a mean case; what about case studies for one or two specific days?

Authors response: Simulations were averaged over the period from 19th to 28 December (i.e. over 9 days) to reduce uncertainties of measured and modeled input parameter. Furthermore, we restricted the simulations to clear sky conditions and over these 9 days we have discarded around 40 hours during which non-clear sky conditions took place. For these reasons we prefer to discuss simulations and observations averaged over a few days.

Reviewer comment: Fig.6 : why does the figure mix a simulated value (at 7cm below the snow surface) with observed values?

C13155

Author response: The firn air mixing ratios at a depth of 7 cm are absolutely needed in our study to calculate HCHO snow fluxes on the base of firn air/air gradients, since the maximum of HCHO in firn air is assumed to be located 7 cm below the surface and a constant diffusivity coefficient is assumed in calculations (see discussions in section 5.2). In the absence of measurements at 7 cm below the surface, values were therefore extrapolated from those observed at deeper depths.

Technical Comments Reviewer comment: P32032, L16 and 19: 29 or 28 December?

Author response: OK right, we changed to 28 December.

Reviewers comment: Several figures currently are difficult to read (small and often the colors are difficult to distinguish, especially for figure 2).

Authors response: We agree that some figures are rather complex and difficult to read as they stand. We here took special care that the print quality of the final figures is improved and that their printing size is more adequate.

Anonymous Referee #2

Reviewer general comment: The manuscript presents a state of art study of HCHO measurements in ambient air, snow, and interstitial air at Concordia in Antarctica during Austral summer. The authors derived the flux of HCHO from snow from vertical gradient measurements. The authors used additional model simulations to drive their conclusions about the HCHO budget. The topic is well suited for publication in ACP. However some sections need to be improved in their logic in order make the manuscript more easily understandable.

Reviewer comment:- There is no real delimitation between the part about experiment, model, field campaigns. . . and the part about results and discussion and this is making the reading not so easy.

Author response: The paper was structured in 6 sections including 1. Introduction, 2. Methods and field campaigns, 3. HCHO in Ambient air, 4. HCHO in the snowpack,

C13156

5. HCHO snow emissions, and 6. Source and sinks of HCHO at Concordia. While delimitations are clear between section 1, 2, 3 and 4 (the two latter being obvious related to results) to make clearer delimitations with sections 5 and 6, section 5 was recalled "Estimates of HCHO snow emissions at Concordia" and section 6 "Sources and sinks controlling the atmospheric budget of HCHO at Concordia".

Reviewer comment: I also suggest reorganize the first part about measurements description: Section 2.1 is common to both field campaigns, right? If yes add a sentence about that. Section 2.2 and 2.3: There is a mix between measurements description, first results and field description (location, metrological data. . .). I suggest if it is possible to include a part about measurement description (if possible with a table with the common parameters between the 2 fields (altitude, depth of measurements, precision, flow. . .) separating between air and snow measurements.) and a part with the field campaign description (location, metrological condition. . .) and particularity of each field campaign in the measurements.

Author response: We added an introduction paragraph in section 2 in which we explain how this experimental section is structured. Indeed when starting to write the manuscript we also thought on a structure which is organized with respect to the different measurement made. However, this would have led to an even more complicated structure, since the analytic conditions are even not the same for the same measurement category. Similarly, since the sampling site at the Dome C station was not the same, thus for example meteorological conditions, which potentially contaminate measurements, are also not the same over the two campaigns. Therefore we believe that the easiest way is to present the two different experiments following the structure we used. We added the following at the beginning of section 2: "Data presented in this study were obtained during two summer field campaigns having taken place at Concordia located on the high East Antarctic plateau (75°06'S, 123°33'E). The 2011/12 campaign conducted from late November 2011 to mid-January 2012 (i.e., the second OPAL field campaign) was mainly dedicated to document HCHO levels at two differ-

C13157

ent heights in the air above the snow surface and to do a few HCHO measurements in interstitial air and in snow. During the 2012/13 campaign (December 22nd 2012 to January 25th 2013) HCHO was measured at different heights in air and firn in the framework of the snow tower experiment SUNITEDC (Evolution du Sulfate et du Nitrate de l'air et de la neige de Dôme C). Hereby the priority was to gain a detailed picture of the HCHO distribution in the interstitial air of the snowpack. In the following section we first describe the analytical method used to measure HCHO. Then, for each campaign we present on site measurement set up and applied working conditions, as well as achieved detection limits in air, interstitial air and snow (Sect. 2.2 and 2.4). Finally, the model used to discuss the different source contributions to the atmospheric HCHO budget at Concordia are briefly introduced in Sect. 2.4."

Reviewer comment: Section 2.2: "Two major North wind direction periods took place": 2 comments: Why do you not consider the episode between the 18/12/11 and 20/12/11? Not long enough or does it not influence the HCHO measurements? I am confused with the wind direction. Maybe I do mistake or we use another convention to read wind direction, but a wind from North have a direction of 180°. So for me, on the 01/01/2012, the direction is 300°-360° so it is a wind from the South-East to the North-West. But maybe I use a different convention or I made a mistake.

Author response: On page 5 Line 32 we defined the North wind direction: "However, several episodes (spanning 18% of the total time) with wind blowing from North (from 30°W to 60°E sector, i.e. the direction of the station) were encountered". Thus station contamination (i.e. North wind direction) is potentially given for wind directions > 330° and < 60° in figure 1 c. In view of that, between 18th to 20th December, the time the wind direction could have brought contamination to the measurements site was very limited. Since no unusual HCHO values were detected we do not assume that our measurements were subjected to a contamination during this period. We clarified in the text that we only removed data due to contamination when the wind was north and the HCHO data set scattered: "Two major North wind periods took place from

C13158

December 30th to January 1st in the morning and most of time after January 9th (Fig. 1c). Since during these events, scattered HCHO values were often observed we cannot exclude a contamination from the station, and therefore the corresponding values were removed from the data set (see red points in Fig. 1a). “

Reviewer comment: Section 2.4: How is the model initialised for CH₄, BrO, OH fields. . .? I suggest to put here the part situated page 32049 line 11 to 26.

Author response: You are absolutely right and we moved the respective lines to section 2.4.

Reviewer comment: Section 3: 2 comments about this part: Field campaign on Dec 2012/Jan 2013 are not discussed in the part as you said in section 2.3. So I suggest to not include reference to this campaign in this part and change the title to “Ambient air of HCHO mixing ratio at Concordia in summer 2011-2012”.

Author comment: Ok we changed the title of section 3 to “3. Ambient air HCHO mixing ratio at Concordia in summer 2011/12”

Reviewer comment: You clearly state that the emissions will be discussed on section 6 but you repeat it at the end of this section. You should only discuss about air measurements and not flux results as you did for section 4 about snowpack.

Author response: Ok, we agree and remove the last sentence of section 3.

Reviewer comment: Section 4.3.1: At the end, you speak about the slope of the linear regression, could you please add your value of the slope or the expression of the Q(T) constant?

Author response: Ok, the value of the slope of our regression is given now in the text and it reads now: The slope of the linear regression obtained with data at -20 cm in the Arrhenius law in Fig. 7 (2.18 with R² = 0.5), for which a large range of temperature is encountered, is quite similar (only 20% higher) than the one of the thermodynamic equilibrium calculated by Barret et al. (2011a).

C13159

Reviewer comment: Section 5.1: You calculate the flux of HCHO from the MOST theory. You compared the flux between two periods but you did not compare the wind speed to interpret the difference between both fluxes. Is the gradient in vmr between 1m and 1cm not influenced by the wind speed?

Author response: The wind speed is in fact included in calculations of the HCHO fluxes via the friction velocity u^* , used to calculate the fluxes.

Technical comments: Reviewer comment: You used ppbv, ppbc and ppbw, I am familiar only with ppbv, it will be appreciable to have once in brackets the definition of these parameters.

Authors response: Ok, we have now defined the units ppbv, pptv, ppbw, and ppbC each when they occurred for the first time in the manuscript.

Reviewer comment: Fig 2: Are the detection limits are available for this field campaign?

Author response: The HCHO detection limit of the 2012/13 experiment are reported and discussed in the text of section 2.3: “Taken as twice the standard deviation of zero measurements, the detection limit was 67 ± 22 pptv from December 22nd to January 6th (151 zero measurements) and 120 ± 55 pptv from January 6th to 25th (185 zero measurements). Compared to other experiments performed with the device (see Sect. 2.2) these rather high detection limits were due related to a frequent presence of air bubbles in the analyzer lines.”

Reviewer comment: Fig 2: the scale used for the panel a) should be between 0 and 400 pptv (as in Fig1 a) or are there data higher than 400 pptv?

Author response: No there are no data higher than 400 pptv. The scale used in Figure 2 a was chosen to be 600 to leave enough space for writing the figure legend. Note also that atmospheric data of this campaign are not further discussed in the text.

Reviewer comment: Fig 4: January 1998 corresponds to Hutterli et al. (2002) study, right? There is no relation between plot and caption.

C13160

Authors response: Ok you are right, the figure caption was reworded accordingly: "Fig. 4. (a) Vertical profiles of HCHO in bulk snow at Concordia. The vertical snow profiles of HCHO obtained from the two snow-pits dug during the 2011/12 campaign are compared to those from a snow-pit dug in January 1998 (Hutterli et al., 2002). (b) Sodium versus HCHO content in the upper 30 cm of the two snow-pits dug in 2011/2012."

Reviewer comment: Fig 7: The characters and psym are too small or the scale not adapted.

Author response: Yes and this figure has been improved.

Reviewer comment: Fig 9: You put observed HCHO, but you do not indicate for which campaign and period, is it an average for the overall measurements?

Authors response: The figure legend was changed following your comment: "Fig. 9. Diurnal cycles (hours are in LT) for the period from December 19th to December 28th 2011 of: (a) HCHO simulated (squares) and observed (red circles) mixing ratios, grey open squares refer to values simulated when only the gas phase chemistry is considered whereas solid black squares refer to values simulated when both gas-phase chemistry and snow emissions are considered (see Sect. 6). The vertical bars reported on simulated values correspond to uncertainties related to the daily variability and calculation uncertainties of parameters reported in Fig. 8. (b) Simulated HCHO contributions of the different gas-phase mechanisms. (c) Contribution of the different uncertainties making up the vertical error bars in (a)."

Reviewer comments: Table 2: 129 pptv (in the table) or 130 pptv (in the text) P 32037, line 16: sect. 2.3 and not 2.2 P 32040, line 7: 1999 (in the text) or 1998 (in Fig 4) Add references to Salmon et al. (2008), Jacobi et al. (2001), Albert (2002), Schwander et al. (1989), Wagner et al. (2002), Eisele et al. (2008) in the final references. The reference France et al. is cited in the text in 2012 (p 32045, line 5) and in the reference 2011. Is it the same article?

C13161

Author response : Ok all done!

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 32027, 2014.

C13162