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Interactive comment on “A reconstruction of the past trend of atmospheric CO based on firn air samples from Berkner Island, Antarctica” *by* S. S. Assonov et al.

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We thank the reviewer for providing comments on our paper. At the time of submission, no data for past trends in the SH based on firn air had been published in the peer reviewed literature. This, despite the generally well acknowledged major significance of CO for the chemistry of the background troposphere. One reason is to be sought in the difficulty of CO measurements, and here we point out the slow process since MAPS in obtaining accurate data of atmospheric CO. This means that even trends over the past 2 decades have some uncertainty. We point out that there is no consensus between the Cape Grim data and the NOAA/CMDL data. We point out that there have been discrepancies between the absolute method (this means a method not dependent on a standard, Brenninkmeijer, 1993; Brenninkmeijer et al., 2001) and other methods for measuring the CO mixing ratio in air (e.g. Novelli 1999; Novelli et al., 1998a, 1998b; Novelli et al., 2003). Apart from the difficulties in measuring CO accurately over a long term in air, we call to attention the difficulties of firn air analysis for CO. Indeed, many trace gas histories have been reconstructed, but not that for CO.

We are content with the referees' acknowledgement of the analytical quality of our data. Notwithstanding, our paper is the first step to reconstruct past SH CO. Our data show lower CO levels at depth, and there is only one explanation, namely CO has been increasing over the past ˜100 years. The question that arises is how actually did CO increase? We do see in recent records based on measurements in air, the evidence for the occurrence of interannual variations. It is consensus, that apart from the Mt. Pinatubo eruption in June 1991, these variations are due to biomass burning variability. Changes in biomass burning related to El Niño events may cause variations, yet substantial changes in the combined CO source over periods of typically decades are a priori not likely. Therefore, one expects a gradual increase in CO, which is reflected by gradual change in CO in firn, which can be properly modelled assuming an input function that is relatively smooth (i.e. basically monotonous increase). After 3 expeditions, data of sufficient quality were obtained for a first ever reconstruction of SH CO. To be more exact, we are dealing with CO in the remote SH. Below we will precisely respond to the reviewers comments ("General comments" is mistakenly given twice).

We write in the second sentence: "All three gases have been increasing rapidly over the previous century mainly due to human activity." In the first sentence we list the gases, namely CO2, CH4, and N2O. The referee writes "The second sentence in the manuscript "A reconstruction of the past trend in CO states that CO has been increasing rapidly over the past century". This is a mistake, we did not write what the referee states we have written. We have no further comment on this statement by the referee.

We have no comment on the subsequent 3 praising sentences, but recall the fact that isotope measurements of CO are considerably more difficult, in particular of 14CO, of which only about 10 molecules per cm3 are present. By analysing the carbon and oxygen isotopic composition, we have a means of verifying the integrity of our samples.

“Nonetheless, only 7 independent data points spanning 1968 to 1995 are used to determine a long-term trend in CO” It is true that only 7 to 9 independent measurements are used. A mistake is the statement “spanning 1968 to 1995”. In firn deposits, air present at any level represent air mixture from a range of ages. The same is true for any trace gas in firn air, which has its own age distribution pattern. Considerably older air is present in the firn near PCOD. Now, one could state that CO has a relatively short lifetime and add to this that sources are fluctuating strongly from year to year (were remind of the fact that CH4 oxidation is an important component in SH CO, possibly rendering relative (and absolute) inter-annual fluctuations smaller than those in the NH. As a result, 7 to 9 data point may not be considered sufficient for determining a long term trend. However, it is the smoothing of concentration variations by processes in the firn air that makes it nearly IMPOSSIBLE to derive shorter term variations. The corollary to this simply is that it makes little sense to have high spatial resolution data in the firn air. Inspection of the data shows that the fluctuations as recorded in the firn are well captured by the 7 to 9 measurements. Importantly, these measurements have been performed on the same scale and thus have not suffered from long-term calibration issues.

“The authors assume that the past trend of CO has been proportional to those of CH4 and CH3Cl.” A method to reconstruct unknown atmospheric trend based on firn data is to run hundreds of random scenarios and select ones producing a best match (the Monte Carlo method, Bräunlich et al., 2001). Instead, we consider another method and adopt two approaches, namely CO proportional to CH4, or CO proportional to CH3Cl. Using CH4 is a logical first choice for SH CO. Using CH3Cl is an independent approach assuming that CO and CH3Cl changes have been mainly driven by biomass burning. As industrial/anthropogenic CO sources in SH are negligible, and there is no evidence for change of natural sources, changes of CH4 and biomass burning are mostly responsible for a CO trend. The fact that two different proxies give similar CO reconstructions, which when used as model input produce satisfactory agreement with observed CO depth profile validates our method. The mistake by the referee renders the ensuing statement "..a serious flaw" difficult and needless to counter.

The referee objects to the justification given for the use of CH4 as a proxy for CO. We give 3 reasons. 1. Photochemical oxidation of CH4 is a major source of CO in the SH. For the present CO burden we give the range of 30 to 40 % based on two independent studies (Manning et al., 1997; and Bergamaschi et al., 2000). This is not contested, and indeed is the overriding argument for using CH4. Thus increasing CH4 mixing ratios will lead to increasing CO. Insofar the increased CH4 burden would lead to reduced OH, this on its own would cause an additional increase of CO, but we leave this out of our discussion. Does one wish to deny this argument? The second reason we give is that the CH4 trend is well known. The referee writes "cannot be supported by available data". It is unclear what is meant here with "available data". Our data for our 3 firn air expeditions show unequivocally the well known increase in CH4. But beyond that, the increase in CH4 is well documented by others (e.g. Etheridge et al., 1998; Ferretti, et al., 2005). Or does the referee mean other data. Whatever, our argument for using CH4 is that its trend is well known and that it is the single major precursor for SH CO. What other trends could be used in the method taken? Our point 3 is that CH4 has been increasing due to anthropogenic activity. We are sure this is true. Insofar anthropogenic activity (industry, fossil fuel burning and anthropogenic NMCH) also contributed to SH CO be it in limited magnitude (Manning et a., 1997; and Bergamaschi et al., 2000), the methane trend may be used as the first approximation to represent all other anthropogenic emissions. The only weak point is that biomass burning components of CO are accompanied by much less production of CH4 (Andreae & Merlet, 2001). To summarize our argument: CH4 is a major source of SH CO and CH4 has anthropogenic components like CO itself. These arguments render it logical to use CH4 as a proxy. Add to this that CH4 is well known, we have a very defendable choice for constructing scenarios. Besides this we have independently considered CH3Cl as a proxy which reflects biomass burning. There are few, if any other long-term records of biomass burning available for SH.

The referee states “CO emissions have certainly increased since the 1900, but their impact on the atmospheric burden are (sic) still open to debate”. Here we would expect evidence (our results perhaps) to be provided. Our reaction is as follows: It is a mistake to state “CO emissions have certainly increased”. We are dealing with the SH, and which scientist has published data that CO emissions have increased in the SH? Further, photochemical considerations for the background troposphere show that increased emissions of CO lead to an increased burden of CO. There is no debate, and certainly not on this very aspect.

“Measurements of CO and CH4 made during the past 20-25 years show very different trends. CO measured at Cape Point South Africa since 1979 captures no significant trend (Brunke and Scheel), while CH4 has increased in the 1980s and 1990s (Khalil and Rasmussen, Dlugokencky et al.)” This is an important point. CH4 increased steadily until 1980 (e.g. Etheridge et al., 1998; Ferretti et al., 2005) and then its increase slowed in 1980s and levelled off during the 1990s (Dlugokencky et al., 2003). CH4 measurements e.g. at Cape Grim from 1985 to 2004 (http://www.dar.csiro.au/capegrim/image/cg_CH4.png) clearly demonstrate this levelling off.

When CO is not strongly coupled to CH4, it should not be used as a proxy. But we already pointed out that the single main source of CO is CH4. Here we bring the following arguments. First we refer to our opening statement which indicates the uncertainties about trends established. In our opinion, the most solid data are those from NOAA-CMDL, for the period 1993 to 2004. The Cape Point (about 34 0S) record is the longest, but more influenced by biomass burning in Africa and South America. This record (from 1978 to 1987, Brunke et al., 1990) in fact demonstrated an increase of 0.29 ppbv/year. Khalil and Rasmussen (1988) also demonstrate CO increase from 1981 to 1987 in Tasmania and Antarctic. The Cape Grim record from 1985 to 2004

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(Baseline 2001-2002, also http://www.dar.csiro.au/capegrim/image/cg_CO.png) shows in fact a peak in 1987, but long term calibration may still have to be resolved (Langenfelds, private communication, 2004). This record may differ from revised data of NOAA-CMDL (Novelli et al., 2003) showing practically a zero trend of CO in Antarctic from 1994 to 2004. The CO trend at Cape Grim from 1984 to 1991 could not have been decreasing (R. Langenfelds, private communication, 2004), simply because during storage CO in standard cylinders may be only produced but not destroyed. An increase may well have happened, but may not have been captured.

Cape Grim data (Baseline 2001-2002, page 46) demonstrate a positive growth of CH4 in 1980s whereas CO growth rate vary around zero. For these years our approach might have missed some detail of the CO trend. (In fact, we use the CH4 trend as a proxy from 1900 to 1993, after 1993 we incorporate direct observations made in Antarctic by NOAA/CMDL.) Let us estimate how large this discrepancy could be. Taking 1558 ppb for the year 1983 and 1687 for 1993 (annual means of the NOAA/CMDL data for South Pole), and assuming only 30 % of modern CO comes from CH4 oxidation, the corresponding CO increase would be 1.0 ppbv only. Taking 40%, that deviation from the apparent zero CO trend (as shown by Cape Grim data (Baseline_2001, page 46) would be 1.4 ppbv. That means that taking CH4 as a proxy we could miss some CO peaks/variations, of amplitude presumably not more than 1.4 ppbv. When aiming to reconstruct a long-term trend, this is not a significant deviation. Besides, to explain the observed CO decrease with depth, we would unavoidably conclude that CO was even lower in the past then the reconstruction based on the CH4 trend. That simply comes from the mass-balance written as Eqn. 1 in the paper.

The reason for difference in trends of CO and CH4 may come from sources which directly produce CO and only little CH4, e.g. biomass burning. The emission ratio for CO to CH4 is between 9ś3 and 16ś8 mol/mol (Andreae et al., 2001). This means that SH biomass burning CO would behave independently from the CH4 trend. That is why we used CH3Cl as another proxy, which major increasing source is a biomass burning (e.g. Andreae et al., 2001; Keppler et al., 2005 and references in these papers).

Complications due to NMHC and VOC chemistry rated to OH. One has to consider 2 issues. One is that other sources of CO (not related to CH4) may have changed independently. For instance biomass burning and the oxidation of NMHC and VOC behave independently from CH4. Thus despite an increase in CH4 (which has a global budget), SH CO may decrease. This we cannot rule out.

The other issue is that of the sink. Here, decreased OH would mean an increase in CH4, coupled with an increase in CO. The equilibrium value would not change much, but the rate of removal of CO (also from other sources) would reduce. Although changes in OH can have occurred, and may be occurring, and in this way to some degree decouple changes in CO from those in CH4, this is likely to be a smaller effect. (That we also note in the paper, page 10274 and 10278.) If an decrease in OH would be due to an increase in CH4, the coupling between CO and CH4 is enhanced. This assumption is plausible for the low NOx SH environment, and if true implicates an enhance coupling between CO and CH4.

To recapitulate. The referee points out the different trends in CO and CH4 in recent times. We point out that the CO trend is not accurately known for the remote SH. We admit that other sources of CO may have (and are likely to have) changed differently. These sources are mainly biomass burning and biogenic precursors. Only if these two would concomitantly change in a direction opposite to the CH4 increase, the coupling between CO and CH4 would be corrupted. This cannot be ruled out, but this scenario is a priori not very likely.

“Rather than trying to model CO trends far beyond the scope of their data, I recommend the authors focus on the period of their measurements” We have severe problems with this statement. The period of our measurements was 1998 to 2003. The air we are dealing with is a mixture that contains contributions of air from 1900 onwards. It can be seen in figure 5 that 12 % of the CO at 58.88 m is older than 1920 (we point out that the age of air is not the same as the age of a trace gas, see our paper).

General comments (probably meant to be specific comments).

“The statement that because the oxidation of CH4 is the main source of CO in the SH, it is expected that CO also has been increasing is simplistic and neglects the complicated chemistry of CO-CH4-NMHC-OH”. “It may, therefore, be inaccurate” The authors find it hard to answer this comment. We reply that when the main source of CO is increasing, CO will increase, unless most other sources concomitantly do the opposite. This is unlikely. One could propose that when CH4 increases CO decreases, but this is wrong. We note in our conclusions that we cannot make a statement about OH. Indeed, increased OH may only have a marginal effect on CO, as rates of both production and destruction increase. Is our statement inaccurate? In our opinion this statement is true, and sufficiently accurate to be the basis for our approach.

“The page long discussion about 14CO” No, we are not prepared to remove this from the manuscript. This highly complex work was the motivation for using large samples, which has given a range of additional analytical and logistical problems. Furthermore it is of importance of those studying CO to know about 14CO. There are few 14CO data, and this paper is the right place to communicate these to our colleagues. But the statement by the referee that it is a page long discussion is simply wrong. It is ¡ page, with the remainder devoted to other isotopes and in particular 17O analysis.

The uncertainties in the samples at 58.88 m are clearly given in Table 2, and in the footnote thereto.

“The paper derives trends of CO from those of CH4 and CH3Cl using a slight modification of the approach presented in Trudinger. However, Trudinger does not determine a trend beyond the period of measurements.” There is a substantial difference. First, age distributions at Berkner are much broader than those at the firn site studied by Trudinger et al.. Though the CO age distributions at Berkner are rather broad, there is significant contribution of old CO (Figure 5 in the paper) which renders us reconstructing the CO trend beyond the mean age of the deepest sample. We agree that broad age distributions is a certain disadvantage of the Berkner firn site. However, one cannot obtain age distributions unless performing a sampling campaign followed by modelling, with model parameters calibrated on CO2 data of actual firn samples. Second, Trudinger aimed to reconstruct gases which trend is absolutely unknown. In contrast, SH CO source magnitude might have been anticipated to smoothly increase, relate to CH4 oxidation and biomass burning. That we have discussed above.

Altogether, the coupling between CO and CH4 in the SH is not ideal, but CH4 is a logical first choice for reconstructing past CO based on our CO data for firn air.

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