Reply to comment of Anonymous Referee # 2

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April 19, 2014

Thank you very much for your extensive comments and your interest in our research. We have taken your comments into account in the revised version of the paper. Without doubt they have pointed towards unclear parts of our method and discussion. We hope that the revisions that we included have made the paper more clear to its audience and properly describe the assumptions and limitations of the employed method.

1 Major Issues

1.1 Impact

The study is performed thoroughly and comprehensively. However, it is quite descriptive in focus.

For publication in ACP, I am missing a discussion of the impact of LRT on atmospheric chemistry and ozone production over oceans and arctic regions. The authors should extent the respective discussion qualitatively, and might even think of ways how to become more quantitative in their conclusions.

This study uses a lot of assumptions to determine the origin and quantity of NO_2 in long-range tranport events, which makes it a further leap to quantify the impact of this phenomenon.

Unfortunately, the most critical region that is most likely impacted by long-range tranport – the Arctic – does not allow the actual observation of plumes from long-range tranport events arriving in winter and spring because of low sun. This makes quantifying the impact very speculative.

Also, the impact of imported NO_2 on local atmospheric chemistry depends strongly on local concentrations of NO_2 and ozone, among others.

A quantitative analysis of the impacts of long range transport of NO_2 is, thus, beyond the scope of this study.

However, in response to the reviewer's suggestion, we have revised the text to more extensively discuss possible impacts of long-range tranported NO_2 in a qualitative manner.

1.2 NO_x / PAN

NOx combines NO and NO2, with varying NO2/NOx ratios, and NOx is also converted (temporarily or eventually) to other nitrogen containing species (NOy), in particular PAN. This is mentioned in the introduction, but especially the discussion of PAN is rather short, while PAN is probably a key player for the LRT of NOx.

Conversion between NO and NO2 and between NOx and NOy affects the NO2 signal observed from satellite. E.g., while an uplifted plume might contain only few NO2 (but a lot of NO and PAN), the total NO2 might increase if the plume is sinking *down due to PAN decomposition and the shift of NOx from NO towards NO2. Also the effective NOx lifetime might be considerably longer than 4 days due to temporary conversion into reservoir species.*

These effects have to be discussed and kept in mind for the interpretation of e.g. the day-to-day changes of total NO2, the calculation of fluxes, etc.

We agree with the reviewer that PAN is a key molecule for NO_x transport, and we have therefore extended the discussion of the role of PAN in the text. However, PAN eludes our observations and it is thus hard to quantify its impact on long-range tranport in the scope of our study or to contribute new results to the role of PAN in atmospheric chemistry.

PAN will without doubt affect the effective lifetime of NO_2, as it could replenish NO_2 over the course of the transport event or serve as a steady sink which reduces NO_2 lifetime, while its impact decays much more slowly.

When we determine lifetimes of NO_2 in long-range tranports, we now more explicitly remark that this is an estimate of the observed lifetime of NO_2, which might significantly differ from the effective lifetime, taking reservoir species, replenishing by lightning etc. into account.

1.3 Cloud Data

The authors mention FRESCO+ cloud data. In their study, however, they calculate a cloud fraction on their own. I do not understand the motivation for this procedure.

As the authors note, "even small cloud fractions have a strong impact on the air-mass factor". Especially for low cloud fractions, the determined CF value according to eq. 6 strongly depends on the a-priori cloud-free reflectivity, which is just taken from MERIS without further discussion.The authors should clearly motivate their choice of an "own" cloud product, need to discuss its uncertainties, have to compare it to FRESCO cloud fractions, and should discuss reasons for and impact of possible differences.

Oddly enough, in section 6, FRESCO cloud fractions are used instead of the CF from eq. 6, which is quite inconsistent.

In addition to cloud fractions, FRESCO+ provides cloud pressure as well. This information is not considered at all in this study. However, if the NO2 plume is actually located inside the cloud, as assumed, the cloud pressure directly provides NO2 plume altitude information! This should be discussed, and the FRESCO cloud pressure for the identified plumes has to be compared to the plume heights inferred from back-trajectories.

There are several reasons for using our own cloud fraction:

- we think it is preferable to determine the cloud fraction in the spectral regions used for the trace gas retrieval as this simplifies the computation of radiance cloud fractions
- retrieving cloud fractions in our fitting window reduces some problems FRESCO+ has over bright surfaces such as deserts and with sunglint
- independently of this study we are trying to use consistent retrieval approaches for all satellite instruments and this is not possible with FRESCO+ which cannot be applied to OMI data

We would also like to point out that FRESCO+, while being a very good cloud product, is by no means the only available cloud retrieval (there are for example also HICRU, OCRA, SACCURA and the O2-O2 algorithm) and we do not agree with the reviewer that every cloud retrieval needs to be "validated" against FRESCO+ before being used.

Nevertheless we have compared our cloud data with those from FRESCO+ and find

- very good overall correlation
- reduced artifacts over deserts and sunglint regions
- overall slightly lower cloud fractions, by about 5-10% for large cloud fractions
- higher cloud fractions for some combinations of solar zenith angle and solar azimuth

As examples, one day of cloud fractions are compared in Fig. 1 and for one orbit, a scatter plot is shown in Fig. 2.

For scenarios typical of long range transport, the NO_2 is not concentrated close to the surface and thus the cloud impact on the AMF is not as critical as over source regions. Therefore, and because the focus of our manuscript is on LRT and not on a new cloud product, we would prefer not to include the comparison to FRESCO in the paper.

The use of FRESCO+ cloud height information is a good suggestion. A discussion comparing FRESCO+ cloud top heights and estimates from HYSPLIT backtrajectories is now included in the paper. In the case study over the North Atlantic, FRESCO+ and HYSPLIT altitudes are consistent with each other. Near South Africa there is an inconsistency (most likely in our determined backtrajectory) on one observation.

1.4 Lightning

The authors discuss lightning as kind of a side phenomenon which sometimes occurs but is generally irrelevant. While this is probably true in general (i.e. anthropogenic NOx emissions are far higher than the NOx produced from lightning), situations might be systematically different for the investigated LRT events. In this context, it would be very helpful to include lightning observations from continuous, global lightning networks like WWLLN in the systematic analysis.

Wenig et al., 2003, report on thunderstorms coinciding with the transport event originating in South Africa. The same is the case for the example discussed in 5.2: Figure 1 displays the flashes detected by WWLLN, which are coinciding with the NO2, at least on July 9. In addition, FRESCO CP (Figure 2) reveals very high clouds South from Madagascar (far above the plume heights given in table 1).

Also for the case study discussed in 5.3, WWLLN detects a considerable amount of flashes, also over land (see Fig. 3), which coincide well with the NO2 plume.

Thank you for this research! We have missed the thunderstorm in our data. Looking into corresponding WWLLN data reveals that the strong thunderstorm on 09 July 2008 indeed coincides with the plume from the case study. On the following days, the plume and the (much less intense) thunderstorm are not co-located any more.

It is likely that this thunderstorm indeed replenished the NO_2 content of the plume. This might lead to either a slower apparent decay of NO_2 in the plume or even to an increase. The impact will strongly depend on the dominant type of flashes in the thunderstorm, with flashes inside the cloud leading to less but more visible NO_2 and flashes between cloud and ocean leading to more NO_2, albeit shielded from view.

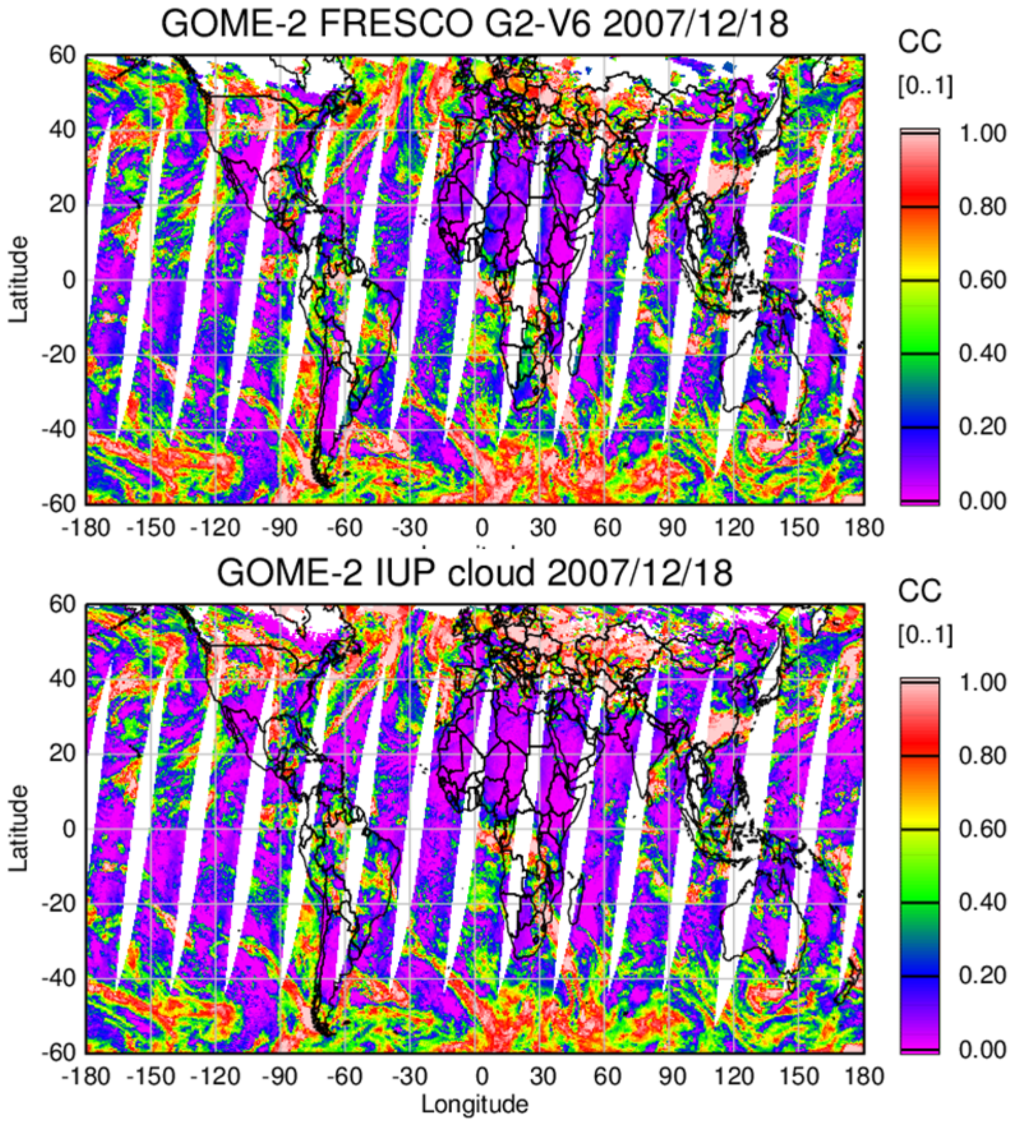

Figure 1: Comparison of FRESCO+ (top) and IUP (bottom) cloud fraction for GOME-2 data from December 18, 2007.

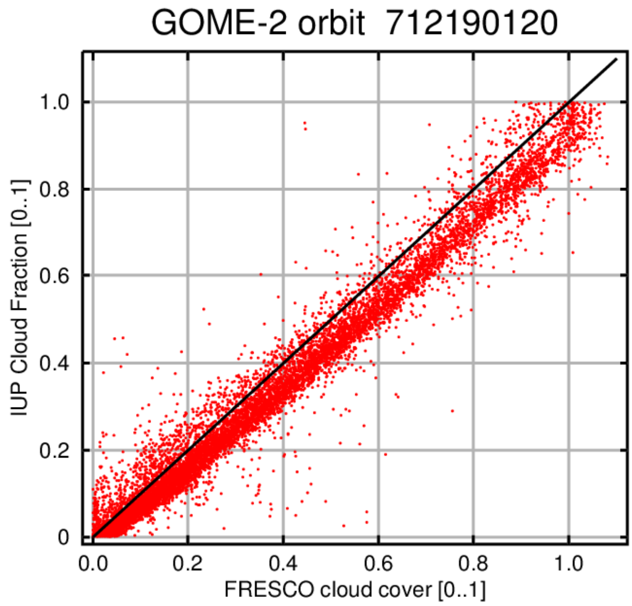

Figure 2: Scatter plot of the IUP cloud fraction compared to FRESCO+ (v6) cloud fraction for one GOME-2 orbit.

We do not have a method to distinguish lightning NO_x from anthropogenic NO_x. The back-trajectory method should filter out many of the potential lightning-only plumes. Replenishing of a long-range tranport plume by lightning can never be ruled out without a deep understanding of the particular thunderstorms.

Browsing through the data we did not detect a strong correlation between lightning flashes and long-range tranport plumes.

From a statistical point of view, the patterns of long-range tranport obtained in this study suggest that thunderstorms are not the cause of the detected events. They may, however, replenish individual events.

In response to the comment made by the reviewer, we have added a section on lightning NO_x, discuss the case pointed out by the reviewer and thereby pay this issue more attention.

> *Besides the production of LNOx, which is indeed hard to quantify and cannot easily be discriminated from the LRT NOx, the role of convective systems, e.g. for the initial uplift of BL NOx into the free troposphere, or the impact on the accuracy of the back-trajectories, has to be discussed.*

The section on the accurracy of backtrajectories has been extended in the text.

2 Minor comments

> *30947/15: Add power plants.*

This issue is now adressed in the text.

> *30947/24: The NOx lifetimes reported by Beirle et al., 2011, are considerably shorter than 8 hours for most Megacities.*

This issue is now adressed in the text.

30948/5: "up to four days" → "up to several days"

This issue is now adressed in the text.

30948/6: "due to lower concentrations of radical species" – and due to higher NO/NOx ratios!

This issue is now adressed in the text.

30948/7: "For it to occur" → "For its occurrence"

This issue is now adressed in the text.

30948/21: PAN plays probably a key role for the long-range transport of NOx. Thus it should be discussed in more detail and perhaps also earlier in this paragraph.

This issue is now adressed in the text.

The conversion of NOx into PAN (and back) also hampers the deduction of the NOx lifetime.

True. It is not even certain if conversion to or from PAN will dominate, leading to either a shortened or prolonged lifetime.

30949/1: What is "common satellite data"?

We refer to cloud filtered data here – most tropospheric NO_2 images in publications or web sites have been cloud filtered. This has been reformulated in the text.

30949/15-17: The discussion of NOx effects on Ozone is quite short and vague. Secion 2 is quite detailed and might be shortened. E.g. the explanation of DOAS (30951/24-30952/17) might be replaced by a reference to Richter et al., 2011.

The discussion on NO_x effects has been improved and section 2 been shortened as suggested.

30955/5: The reference to Eskes and Boersma in this context is strange, as in this study, clouds are treated as Lambertian reflectors, i.e. multiple scattering effects are ignored! There are several other studies which have discussed the different cloud effects, and show Block AMFs similar to Fig. 2.

We agree and have replaced the references by Hild et al., 2001 and Beirle et al., 2009.

30958/22: Ships are "concentrated" NOx emitters on the open ocean!

Indeed. However the high emission rates occur only over a small area, thus not leading to a large transported plume of NO_2 that could be detected in GOME-2 measurements.

30959/13: "developed"

Corrected.

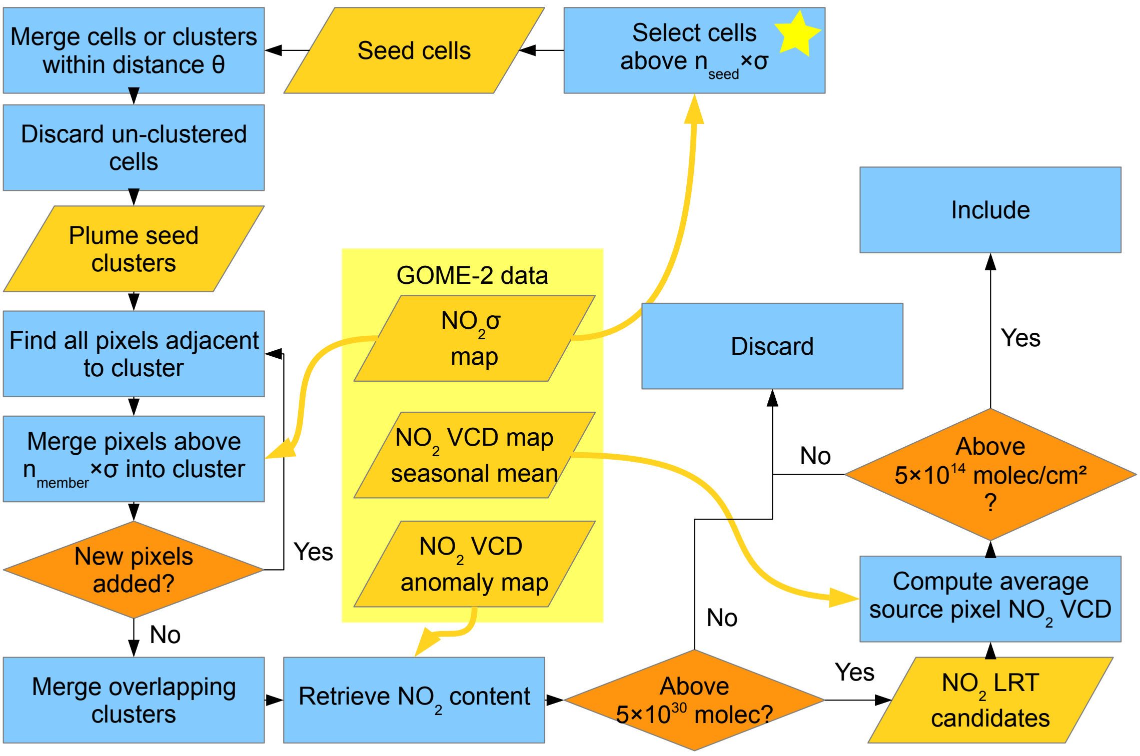

Figure 3: Flow chart illustrating the steps from the prepared GOME-2 data to verified LRT plumes.

> *30960/3-4: This is a too absolute statement: There might be reasons for plumes over oceans without LRT, e.g. a burning oil platform, or strong thunderstorms.*

True. However, these will either not occur on a regular basis or not be concentrated to areas downwind of major emission regions. As individual events, they might lead to false positive detections.

> *30960/8:* $n_{\text{seed}} \times \sigma$

Corrected.

> *Figure 4 is meant to illustrate the selection procedure, but misses several aspects. The identification of plumes consists of "seeds", which are either "merged" or "discarded", with additional "iterations" and changing thresholds (n_{seed} versus n_{member}). All these steps and the different pathways for candidate pixels should be illustrated examplarily.*

We now include a new flow chart in the text (Fig. 3), illustrating the actual algorithm.

> *30960/25: Which kind of instrumental artefact could be interpreted as a LRT plume?*

In some DOAS retrievals for weak absorbers, polarisation calibration issues lead to unrealistically high (or low) slant columns under certain viewing conditions in GOME-2 data. However, as this is not the case for NO_2, we have removed this statement.

30961/4: FRESCO CTP yields information of the cloud altitude, which is assumed to be the same as the NO2 plume altitude.

This assumption is used to derive the NO_2 content of the plume cells, as this is the simplest assumption. For determining the origin of the plume, we relax this constraint to not falsely rule out the actual origin of the plume.

30962/3: Which area was chosen for averaging?

The seasonal average maps are of the same resolution as the maps used to detect long range transports. Each plume cell is tracked back to one pixel in the seasonal average maps. The average of these pixels (duplicates included) is used for this criterion.

30962/6: "All plumes ... are discarded": It would be interesting to know how many plumes have been discarded by this criterion.

Roughly 56% of all detected plumes are rejected and only 44% accepted as being part of long-range transport events.

30962/12: 10e15 molec/cm2 is actually larger than the threshold value given in line 4!

Indeed, it is. However, this means that only the strongest shipping lanes would be treated as sources, if almost *all* trajectories would hit exactly the shipping lane. Due to the accuracy of the HYSPLIT backtrajectories, this is practically impossible.

30964/1: To avoid misunderstandings, I propose to add "as long as the NO2 plume is within the cloud".

Done.

30964/12: FRESCO provides cloud altitude information!?

It does not provide a vertical profile of optical thickness per altitude which would be needed to model a non-homogeneous cloud.

Some meteorological models provide this information which is, however, unreliable if used in conjunction with NO_2 profiles.

30965/7: "high"→"higher"

Corrected.

30965/12: "we perform"→"performed"

Corrected.

30965/14: "eventually"→"possibly" or "probably"

Corrected.

30965/17: "so that stray pixels ...": I propose to skip this.

This passage has been removed from the text.

30967/15-16: I do not understand why high emission rates and long lifetimes should be obstructive for the observation of LRT over several days!?

It is only in the combination of these two criteria that long-range transport events are hard to observe over multiple days. LRTs occur mostly in winter and they tend to move polewards. However, scattered light DOAS instruments cannot observe in polar night.

30967/26: which is difficult anyhow due to changing NO/NOx, formation and decomposition of PAN etc.

This issue is now adressed in the text.

30969/1-3: There are many possible explanations for increasing NO2, e.g. LNOx, conversion of NO into NO2, or decomposition of PAN.

We added a discussion of these factors to the texts.

30970/23: "deceleration"

Corrected.

30970/26: Please reformulate this sentence.

This sentence now reads: This suggests that the NO_2 plume stays compact even after separating from the meteorological phenomenon leading to its emission.

30972/19: Values for m' are derived for each season, but these numbers, their meaning, and potential impacts are not discussed at all.

The revised text now addresses this briefly:

This means that plumes in autumn and winter follow a distribution that leads to much higher NO_2 content than in spring and (derived visually from Fig. 12) in summer. This supports cyclones and low temperatures as favourable conditions for long-range tranport.

30975/10-11: add "... by creating a similar map (Fig. 16)", and skip the last sentence of the paragraph (line 14).

Done.

30975/20: Given the uncertainties of the back-trajectories as discussed in the following paragraph, I see the discussion of "bush fires" as significant sources as rather speculative. According to long-time means, the Highveld area and Johannesburg are by far the dominating source regions over South Africa.

Ideed, they are. This statement serves only to acknowledge that we might also see individual events originating from bush fires. Their overall contribution, however, will be negligible.

30979/9: Isn't that negative anomaly caused automatically by the algorithm? On day+1, the mean is calculated from the days before and after, including day0.

This analysis does not operate on the mean maps that were prepared for the detection of events. It operates on the daily maps of observed NO_2 as shown in Fig. 1.

A negative anomaly is to be expected after an event leaves, however, as a large quantity of NO_2 is removed from the source region by the transport.

30979/25: "Fig. 23 shows no NAO characteristics": I do understand this statement; Fig. 23 shows a very clear dipolar pattern!?

There is a dipolar pattern. However, the low pressure anomaly does not reside above Iceland, as would be characteristic for the NAO.

30980/1-11: Please add a figure of the discussed cloud fraction anomaly.

We removed this passage from the text as a revised study does no longer yield this result.

Fig. 6: "indicated by purple circles": → add "in the center and right columns".

This issue is now adressed in the text.

Fig. 19: The observed NO2 flux does not have to correspond 1:1 to the emissions at ground, thus I recommend to change the y-axis label.

The label now reads: NO_2 in LRT events [GgN/a].