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May 23, 2014

To the Copernicus editor
Dr. Van Roozendael

Dear Dr. Van Roozendael,

first of all I want to apologize for the long revisioning process. I have moved to a new job and work on these results in my spare time.

In the last weeks, we have tried to address all the issues found during the reviewing process. Especially, we have extended the section on LiNO_x, analyzed vertical profiles of clouds and NO₂ in MACC data and revised the results from composite analysis and the correlation of European export to NAO phases.

Please find on the following pages the full replies to both editors as well as the \LaTeX diff between the originally submitted and the revised article.

Yours sincerely,

Achim Zien

Reply to comment of Anonymous Referee # 1

Achim Zien

April 19, 2014

Thank you very much for your comments and your confidence in our research. Your comments have been taken into account in the revised version of the paper and without doubt have pointed towards unclear parts of our method. We hope that the revision made has made the paper more clear to its audience.

1 Cloud and NO₂ profile

In section 2.1, the authors present their approach to retrieve VCDs in partially cloudy scenes, and the limitations of their approach to calculating AMFs are discussed in Section 4.2. As the authors indicate, the air-mass factor depends on where in the vertical direction the trace gas is situated, and this becomes even more significant when clouds are in the scene. My one major concern is that the authors appear to base their assumption about the vertical distribution of NO₂ in cloudy scenes on one single set of observations (the TRACE-P campaign). Therein, it was found that CO tends to be homogeneously mixed inside the cloud, resulting in those cases from the passage of a cold front over an emission region. While this phenomenon may be typical of initiating long-range pollutant transport over China (which is indeed eventually re-confirmed by the algorithm), I wonder how appropriate it is to apply systematically across all cases of cloudy scenes.

The TRACE-P observations were taken right along the Asian Pacific Rim; but the authors of the present paper do not explain why the vertical distribution of NO₂ in the presence of clouds will remain constant from the coast to the open ocean. Further in the paper, the authors discuss the issues resulting from the chaotic movement under conditions of strong winds (l. 710); can this alter the appropriateness of the homogeneously mixed profile at cloud height? It may be that the authors cannot find examples of other field data to confirm or deny to existence of other vertical distributions in the presence of clouds, but the fact that their choice is based on a single reference from a single region of the world targeted for specific meteorological dynamics is not given enough attention or discussion. What do modeled NO₂ profiles over the oceans look like when clouds are present? While they may not be entirely accurate, their variety may lend some insight into the appropriateness of the single profile that is being assumed in this paper.

We agree with the reviewer that the assumption on the NO₂ profile is critical and that we have taken a very rough approach by assuming a well-mixed profile colocated with the cloud. Unfortunately, there is to our knowledge no measurement of both NO₂ and cloud profiles in long-range transport events, and only few trace gas and cloud profile measurements in long-range transports at all. This is, why we used the TRACE-P measurements.

The reviewer suggests using model profiles in order to evaluate the development of NO₂ profiles during long range transport events. At the beginning of our project, we tried to use GEOS-Chem model output as a priori for our retrievals but had to realise that the representation of long range transport events in the model did not match well with observations of both clouds and NO₂ in the satellite data. A model like WRF-Chem will probably perform much better but such data is not available for multiannual global runs as would be needed here. In response to the comment made by the reviewer, we have investigated data from the MACC reanalysis (Inness et al., 2013, doi:10.5194/acp-13-4073-2013) which has a reasonably high resolution of about 1.25×1.25 degrees. For one of the examples discussed in the paper (October 2nd, 2010), the model NO₂ field reproduces the observed export pattern at least qualitatively (see Fig. 1). In Fig. 2, three exemplary NO₂ profiles are shown, indicating that the model predicts a relatively well mixed layer of NO₂ with a layer top altitude increasing with distance from the source. The model clouds (here approximated by the sum of liquid water and ice content) show a very similar behaviour with the exception of the missing values below cloud base. In this case, our assumption of similar behaviour of cloud and NO₂ is justified but the assumption of a layer between 3 and 5 km is not. As discussed in the paper, the vertical position of such a cloud does not have a very large effect on the AMF as long as the NO₂ is well mixed within the cloud.

This rather anecdotal confirmation for our approach could in principle be repeated on other cases but is a very manual and subjective process where individual events have to be identified in the model data, pixels be selected, and profiles be compared visually. We therefore do not think that adding some more random cases would make our argument much stronger and cannot conceive an automated way to analyse the link between cloud and NO₂ profiles in LRT events in model data as a function of transport time.

We do however appreciate the point made by the reviewer and have extended the discussion on the uncertainties introduced by our assumption.

2 Cloud-free and cloudy AMF

Along the same lines, it is not clear to me how the total AMF is always calculated by combining the weighted cloud-free and cloudy AMF. It does seem that the only realistic choice is to assume the same NO₂ vertical profile is used in calculating the cloudy and cloud-free air mass factors for a single pixel– But I am wondering about situations whether the pixel is partially cloudy. The calculation of the radiance cloud fraction seems to force the authors to assume that in the presence of any cloud fraction, no matter how small, the result is a pixel where the NO₂ distribution is homogeneously mixed at the determined altitude of the cloud. What about pixels where the radiance cloud fraction is very small– wouldn't it be better to apply the standard profiles in those cases? Is this done? Is there a radiance fraction cut-off (or should there be?) where the trace gas profile is assumed to be standard vs. homogeneously mixed at one altitude? If there is, it is not clear to me– perhaps I have missed something in the manuscript.

The objective of this study is to investigate long range transport events, and through the analysis applied, we try to select only those observations which are part of such events. We therefore decided to use dedicated AMFs which are as appropriate as possible for LRT events but will not necessarily be correct for other situations.

The NO₂ is – for the purpose of calculating the AMF – always assumed to be at the same altitude: between 3 and 5 kilometers. Assuming that the NO₂ is elevated (as is necessary for NO₂ long-range transport) the changes in AMF are relatively small when moving the NO₂

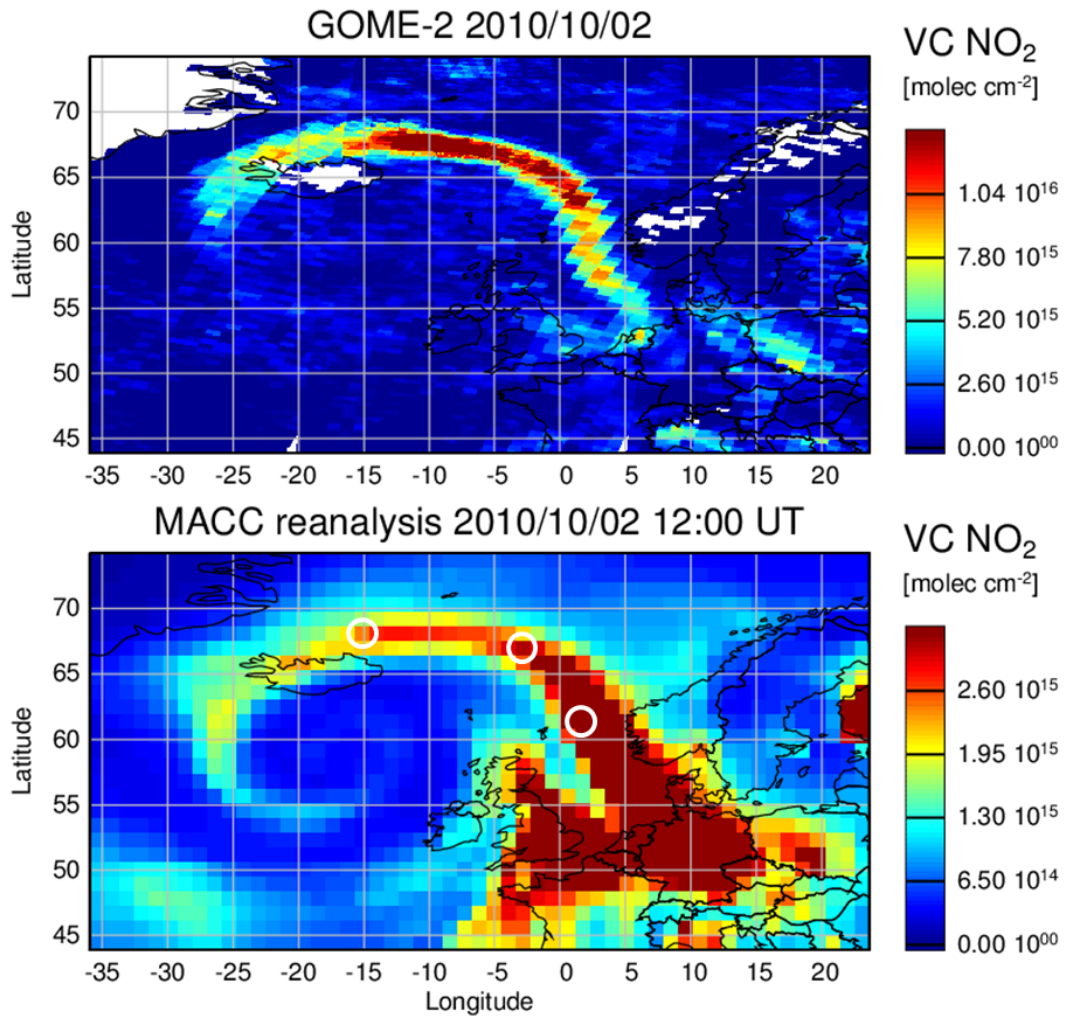


Figure 1: Long range transport event on October 2, 2010 as seen in GOME-2 data (top) and the MACC reanalysis (bottom). Please note the different colour scales. The three circles in the lower plot indicate the pixels for which vertical profiles are shown in Fig. 2.

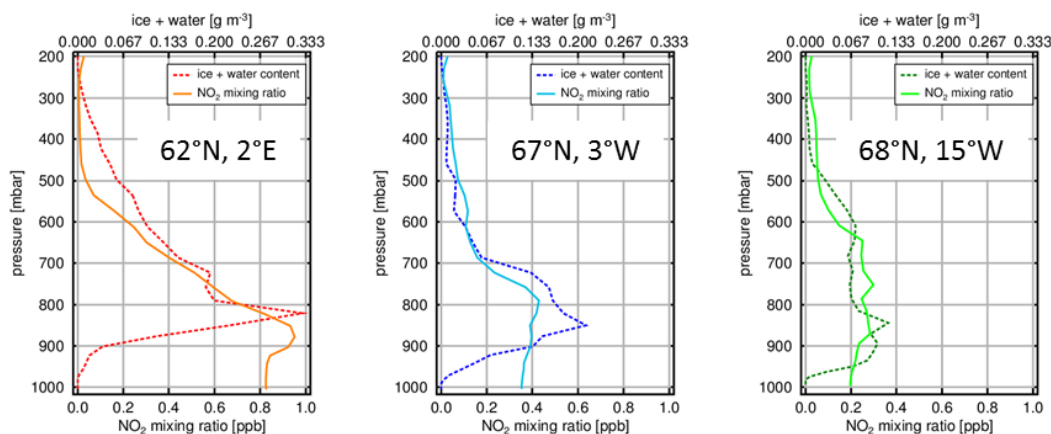


Figure 2: Vertical profiles of NO_2 and cloud liquid water and ice content for three geolocations in the MACC reanalysis output for October 2, 2010.

further up or down. For the cloudy AMF, the cloud is also simulated at an altitude of 3 to 5 kilometers. Thus we assume that the NO_2 in a partially cloudy pixel is homogeneously distributed. In our opinion, this is the most consistent assumption although – as the reviewer correctly points out – it will not be appropriate in pixels not affected by LRT. However, we hope that such pixels will be eventually removed from the analysis which tries to isolate LRT events.

The text has been updated to clarify our approach. In response to the first comment of the reviewer, the impact of locating the NO_2 at the wrong altitude is now discussed in more detail in the paper.

3 Technical comments

l. 882-884: Is this statement (regarding NO_2 and glyoxal from bush fires) based on the present work, or presented in the literature? Please include references if necessary.

References for the detection of glyoxal from satellite are:

- Wittrock, Folkard, Andreas Richter, Hilke Oetjen, John P. Burrows, Maria Kanakidou, Stelios Myriokefalitakis, Rainer Volkamer, Steffen Beirle, Ulrich Platt, and Thomas Wagner. 2006. „Simultaneous Global Observations of Glyoxal and Formaldehyde from Space“. *Geophysical Research Letters* 33 (16): L16804. doi:10.1029/2006GL026310.
- Vrekoussis, M., F. Wittrock, A. Richter, and J. P. Burrows. 2009. „Temporal and spatial variability of glyoxal as observed from space“. *Atmos. Chem. Phys.* 9 (13): 4485–4504. doi:10.5194/acp-9-4485-2009.

l. 1206: spelling of instead

This has been fixed in the text.

l. 1651-1661: This reference made it out of ACPD into ACP long ago– why not reference the ACP published version?

All ACPD references have been updated, if possible.

Reply to comment of Anonymous Referee # 2

Achim Zien

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 extend 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 NO₂ in long-range transport 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 transport – the Arctic – does not allow the actual observation of plumes from long-range transport events arriving in winter and spring because of low sun. This makes quantifying the impact very speculative.

Also, the impact of imported NO₂ on local atmospheric chemistry depends strongly on local concentrations of NO₂ and ozone, among others.

A quantitative analysis of the impacts of long range transport of NO₂ 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 transported NO₂ in a qualitative manner.

1.2 NO_x / PAN

NO_x combines NO and NO₂, with varying NO₂/NO_x ratios, and NO_x is also converted (temporarily or eventually) to other nitrogen containing species (NO_y), 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 NO_x.

Conversion between NO and NO₂ and between NO_x and NO_y 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 NO_x from NO towards NO₂. Also the effective NO_x 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 transport 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 NO₂, as it could replenish NO₂ over the course of the transport event or serve as a steady sink which reduces NO₂ lifetime, while its impact decays much more slowly.

When we determine lifetimes of NO₂ in long-range transports, we now more explicitly remark that this is an estimate of the observed lifetime of NO₂, 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 NO_x emissions are far higher than the NO_x 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 NO_2 , 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 NO_2 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.

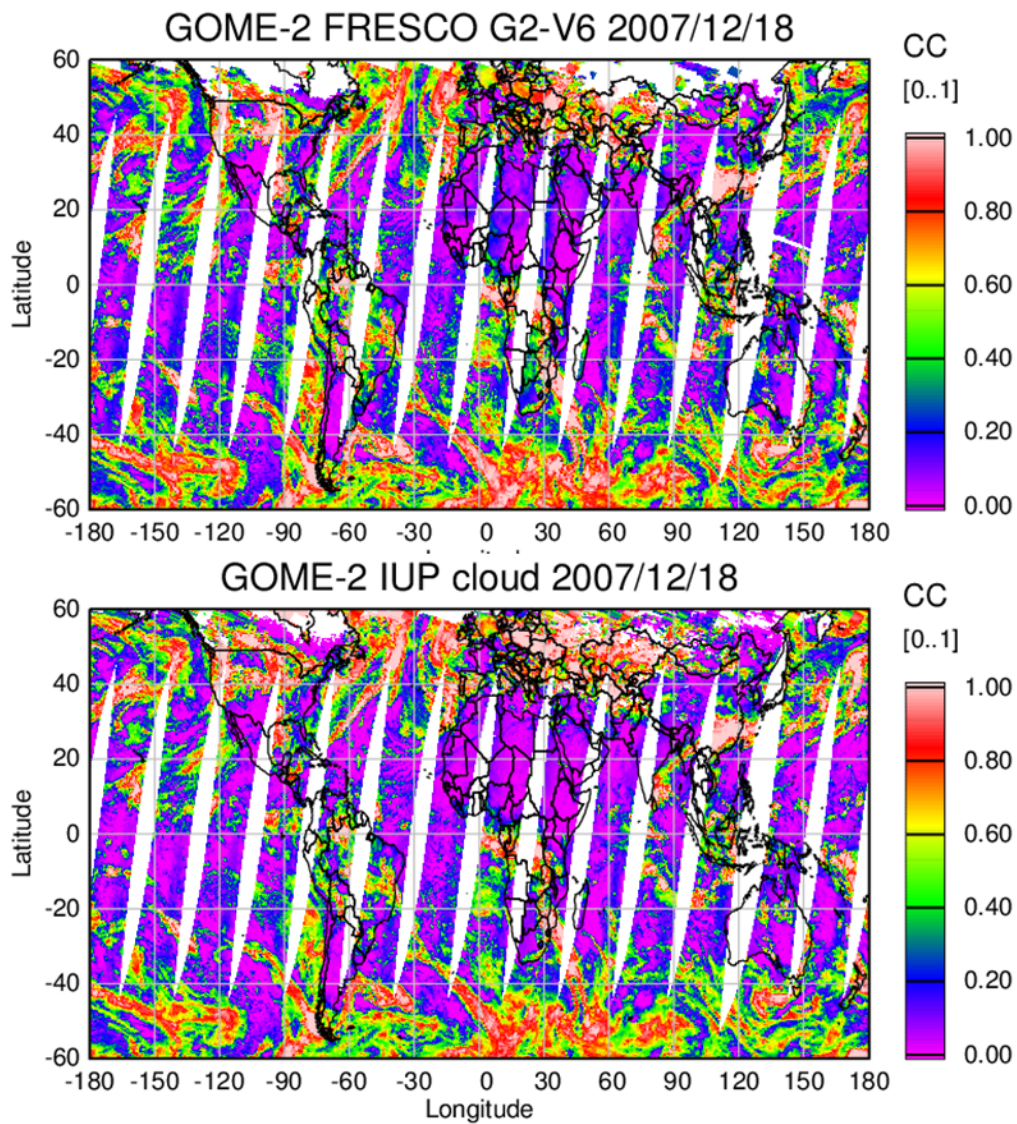


Figure 1: Comparison of FRESKO+ (top) and IUP (bottom) cloud fraction for GOME-2 data from December 18, 2007.

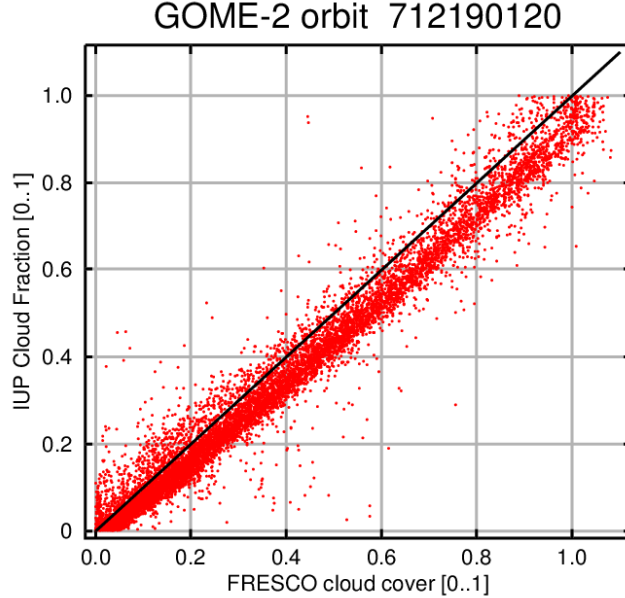


Figure 2: Scatter plot of the IUP cloud fraction compared to FRESCO+ (v6) cloud fraction for one GOME-2 orbit.

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 transport 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 transport plumes.

From a statistical point of view, the patterns of long-range transport 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 LNO_x , which is indeed hard to quantify and cannot easily be discriminated from the LRT NO_x , the role of convective systems, e.g. for the initial uplift of BL NO_x into the free troposphere, or the impact on the accuracy of the back-trajectories, has to be discussed.

The section on the accuracy 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 NO_x lifetimes reported by Beirle et al., 2011, are considerably shorter than 8 hours for most Megacities.

This issue is now addressed in the text.

30948/5: “up to four days” → “up to several days”

This issue is now addressed in the text.

30948/6: “due to lower concentrations of radical species” – and due to higher NO/NO_x ratios!

This issue is now addressed in the text.

30948/7: “For it to occur” → “For its occurrence”

This issue is now addressed in the text.

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

This issue is now addressed in the text.

The conversion of NO_x into PAN (and back) also hampers the deduction of the NO_x 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 NO₂ images in publications or web sites have been cloud filtered. This has been reformulated in the text.

30949/15-17: The discussion of NO_x effects on Ozone is quite short and vague. Section 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” NO_x 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 NO₂ that could be detected in GOME-2 measurements.

30959/13: “developed”

Corrected.

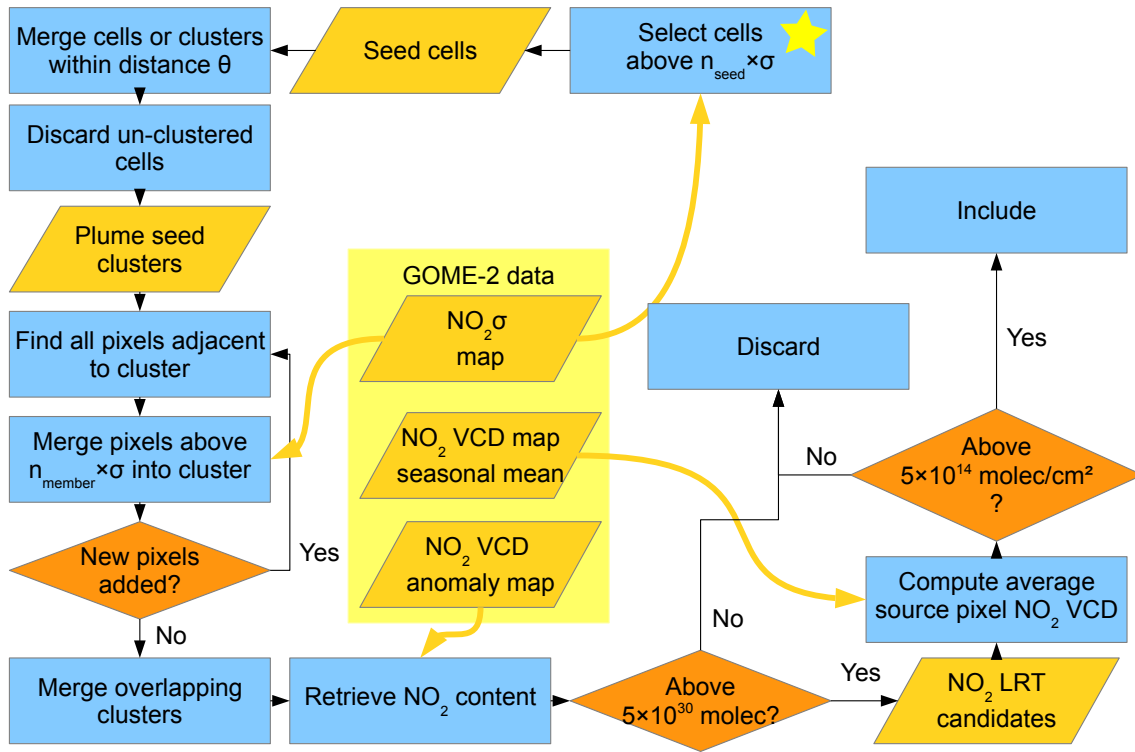


Figure 3: Flow chart illustrating the steps from the prepared GOME-2 data to verified LRT plumes.

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 exemplarily.

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 NO₂ 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 NO₂ 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/NO_x, formation and decomposition of PAN etc.

This issue is now addressed in the text.

30969/1-3: There are many possible explanations for increasing NO₂, e.g. LNO_x, 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 NO₂ 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 NO₂ content than in spring and (derived visually from Fig. 12) in summer. This supports cyclones and low temperatures as favourable conditions for long-range transport.

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 NO₂ as shown in Fig. 1.

A negative anomaly is to be expected after an event leaves, however, as a large quantity of NO₂ 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 addressed 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: NO₂ in LRT events [GgN/a].

Systematic analysis of tropospheric NO₂ long-range transport events detected in GOME-2 satellite data

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Abstract. Intercontinental long-range transport (LRT) events of NO₂ relocate the effects of air pollution from emission regions to remote, pristine regions. We detect transported plumes in tropospheric NO₂ columns measured by the GOME-2 / MetOp-A instrument with a specialized algorithm and trace the plumes to their sources using the HYSPLIT lagrangian transport model. With this algorithm we find 3808 LRT events over the ocean for the period 2007 to 2011. LRT events occur frequently in the mid-latitudes, emerging usually from coastal high-emission regions. In the free troposphere, plumes of NO₂ can travel for several days to the polar oceanic atmosphere or to other continents. They travel along characteristic routes and originate from both continuous anthropogenic emission and emission events such as bush fires. Most NO₂ LRT events occur during autumn and winter months, when meteorological conditions and emissions are most favorable. The evaluation of meteorological data shows that the observed NO₂ LRT is often linked to cyclones passing over an emission region.

1 Introduction

The transport of atmospheric pollution over long distances mostly affects long-lived species, such as CO, SO₂ and O₃. During long-range transport (LRT) of chemical species, trace gases are transported over intercontinental distances, relocating gases from emission to remote and pristine regions. As a result, air pollution has to be regarded as a global instead of a local phenomenon. Under certain conditions, this can also affect short-lived species which are commonly considered to be bounded to their emission regions.

While long-lived gas species can also mix slowly in the atmosphere to reach remote regions, a short-lived species has to travel fast before it is eventually converted into other species.

Here, we investigate the long-range transport of NO₂. Its lifetime in the planetary boundary layer (PBL) amounts to a few hours, depending on the strength of solar irradiation and on the available radical species. This, combined with low wind speeds near the surface, makes long-range transport of anthropogenic NO₂ in the planetary boundary layer very unlikely.

Still, satellite observations of NO₂ frequently exhibit such long-range transport events and allow a systematic analysis of their properties – such as their NO₂ content, altitude and age.

NO₂ is a toxic trace gas which can harm respiratory organs. A major fraction of the emissions takes place in the form of NO which then rapidly converts to NO₂ until the Leighton photostationary state is achieved at a ratio of NO/NO_x ≈ 0.2–0.8 (?) – depending on radiative flux, available radical species and air pressure. NO_x is defined as the sum of the species NO and NO₂.

NO and NO₂ emissions originate from various sources. The dominant sources are anthropogenic emissions from combustion processes in transportation, power plants, industry and agricultural biomass burning, as well as natural sources such as lightning emissions, natural biomass burning and microbial soil emissions. ? report a total yearly NO_x emission rate of 43 TgN/a in 1996–1997, with anthropogenic sources contributing roughly half of the emissions.

NO₂ ~~harms respiratory organs.~~ It also reacts with OH to form HNO₃ which permanently removes the NO₂ from the air masses and results in acid rain. This is the major atmospheric loss of NO₂. Besides that, NO₂ directly impacts the ozone cycle in the troposphere, where it favors O₃ production. The presence of OH and volatile organic compounds (VOCs) can amplify this effect leading to the well known photochemical ozone smog. As the lifetime of NO₂ is relatively short, ozone smog formation is usually limited to polluted regions. However, in air masses containing large

amounts of biogenic VOCs, addition of NO_x from lightning, biomass burning or potentially from long-range transport can also lead to ozone production. At very large NO₂ concentrations, ozone formation is suppressed leading to lower ozone values in pollution hotspots.

The lifetime of NO₂ ranges from around 8 hours in a typical planetary boundary layer scenario to a few days in the upper troposphere (??).

A long-range transport (LRT) event denotes a distinct plume of trace gas being exported from an emission region to a downwind region over a long distance, typically several thousand kilometers. While long-range transport could, in principle, take place in the boundary layer, it is more likely that the actual transport happens after convection out of the planetary boundary layer into the free troposphere, where wind speeds are much higher, due to a lack of interaction with the surface.

For NO₂, long-range transport will predominantly take place in the free troposphere, where – in addition to the higher windspeed – its lifetime is extended to up to four days, due to lower concentrations of radical species. As NO₂ is mainly emitted in the boundary layer, this phenomenon could be expected to be rare. For ~~it to occur~~ its occurrence, there has to be a mechanism to lift polluted air-masses into the free troposphere.

Once this happens, the NO₂ is transported from emission regions to remote, pristine regions, e.g. over the oceans, into polar regions or to other continents. This means that the NO₂ in these cases does not only affect its source region, but has regional or even global impacts.

As this study will show, NO₂ long-range transport plumes can have a horizontal extent of more than 1000 km. Due to this large extent, plumes are subject to horizontal shear winds. This results in filamentation and typical arc-like structures after a few days. The plume will also disperse over the course of the transport, typically after a few days (??).

Due to chemical conversion and physical dispersion and filamentation, intercontinental NO₂ long-range transport events are usually seen departing from an emission region to the ocean, but they dissolve before arriving on another continent. Once lifted, the ratio of NO/NO_x will change leading to a reduction of NO₂ and a larger, unobserved reservoir of NO. Over the course of transport, NO₂ partly is converted into peroxyacyl nitrate (PAN) and other reservoir species, which may then release ~~upon descent over the shore, when concentrations~~ NO₂ upon descent, when concentrations of radical species, pressure and temperature increase (???). This leads both processes, direct long-range transport of NO_x and transport of its reservoir species lead to an effective relocation of NO_x emissions.

NO₂ concentrations are can be observed both via in-situ and remote sensing methods. As long-range transport is a large-scale phenomenon, we use data from satellite remote sensing observations for our large-scale and global analysis.

However, NO₂ long-range transport events are rarely seen in ~~common satellite data~~ most satellite data products. This can lead to the false assumption that they also occur rarely. The reason for this lies in the common practice of filtering cloudy pixels from satellite observations. This is done because clouds complicate the radiative transfer and make the retrieval of trace gas concentrations harder. In particular, the sensitivity to NO₂ in the boundary layer is reduced in presence of clouds for most common observation scenarios.

If we omit the cloud filter, we observe many long-range transport events just by browsing through the data. Due to their intermittent occurrence and rapid movement, such events ~~can only be~~ are best seen in daily or orbit-wise data – not in data averaged over longer time periods.

For different chemical species, long-range transport events have received more attention in the last few years. The Hemispheric Transport of Air Pollutants (HTAP) task force was created to collect data and knowledge on this phenomenon and assess its impact on the environment. In their report (??), they find that a significant fraction of ozone pollution in the Northern Hemisphere is driven by transport from remote sources, mostly of ozone precursors such as methane and NO_x. They expect the resulting increased base levels of ozone to lead to an increased threat to human health and crop yields.

There are a number of satellite based case studies of individual events of NO₂ long-range transport. ? report the first observation of such an event, a plume emitted from South Africa in May 1998. In their study, a high-pressure system favored a localized build-up of NO₂ concentrations which were then rapidly lifted to an altitude of 2–6 km above mean sea level (a.m.s.l.) by a passing low-pressure system. There, longer lifetime and higher wind speeds allowed the NO₂ to travel onto the open ocean.

? investigated an episode in which an explosively developing cyclone transported a significant plume of NO₂ over the Atlantic in about one day. The NO₂ was lifted upwards by a warm conveyor belt (WCB). In a climatological study, they find intercontinental express highways between North America and Europe which are much stronger in winter and can contribute about 2–3 pptv of European NO₂ concentrations during winter.

? discuss an event during which NO₂ from the central German Ruhr area was lifted into the free troposphere (over the course of a day) and transported into the Alps where a significant increase in concentrations was measured in-situ on the Zugspitze and on multiple sites in Switzerland.

Studies by ? and ? illustrate further aspects of individual, observed transport events.

Unfortunately, there are – to our knowledge – no in-situ measurements of tropospheric NO₂ long-range transports by aircraft which would allow us to determine typical vertical concentration profiles and verify the results of this study with non-satellite observations.

? have focussed on modeling NO₂ long-range transport with global chemical transport models (GCTMs). They find that 8–15 % of NO_x emissions are transported over 1000 km from their source regions, using WRF-Chem and CMAQ for rapid vertical transport and MOZART as GCTM. They also note that in most GCTMs, rapid convection (such as in frontal passages) is not adequately represented, which biases the simulation of long-range transport events. The modeling of horizontal transport tends to dilute the plumes' boundaries, which are found to be rather sharp in observational data.

So far there has – to our knowledge – not been a systematic study of NO₂ long-range transport events using observational data. Such studies are ~~necessary~~ necessary in order to judge the impact of NO₂ long-range transport on the atmospheric chemistry in pristine and sensitive environments such as the Arctic and to validate its impact as estimated from GCTMs.

In this study, we have used daily maps of tropospheric NO₂ from the GOME-2 / MetOp-A instrument (Sect. 2). We implemented an algorithm to detect long-range transport events over the ocean in this timeseries of two-dimensional data (Sect. 3). This allows us to perform a systematic study of long-range transport of NO₂. We retrieved additional properties of the detected plumes with backtrajectories from the HYSPLIT lagrangian transport model. We determined the most likely backtrajectory using a scoring system and validated the plume to be a long-range transport event. We further describe the limitations of this study (Sect. 4). After obtaining this dataset, we have performed four case studies on remarkable and typical long-range transports (Sect. 5). We examined statistical properties of the obtained dataset and investigated typical meteorological conditions accompanying the emission of NO₂ long-range transport plumes (Sect. 6).

2 GOME-2 satellite observations

This study uses data from the GOME-2 / MetOp-A satellite instrument, which is converted to daily 2-D tropospheric NO₂ vertical column density maps for further analysis.

GOME-2 (??) are a series of instruments aboard the MetOp satellites which measure trace gas optical depths via differential optical absorption spectroscopy of scattered sunlight (DOAS; ??). The first GOME-2 instrument started operation on 4 January 2007 aboard MetOp-A and provides continuous observations until now. GOME-2 is an improved version of GOME (??) and SCIAMACHY (??).

MetOp-A is on a sun-synchronous orbit at an altitude of 800 km a.m.s.l., giving measurements at roughly the same local time for all sub-polar latitudes. It orbits the Earth 14 times a day on a near-polar orbit ~~in descending node~~ and has an equator crossing time of 09:30 local time ~~in descending node~~. GOME-2 measures in a sweeping-broom configuration, with a pixel size of 80 × 40 km². The swath

width of 1960 km yields a nearly global coverage every day. ~~Backscan-pixels, ascending node pixels and pixels with a solar zenith angle of sza > 80° were excluded from the data.~~

For the DOAS analysis, the optical depth is derived from nadir observations $I_{\text{nadir}}(\lambda)$ and daily solar irradiance measurements $I_0(\lambda)$. Absorption features of trace gases (and other ~~features~~ effects like the Ring-spectrum) are fitted in a suitable wavelength window. The low-variance part is approximated by a polynomial function. The remaining high-variance parts of the measured optical depth are fitted by reference spectra (from laboratory measurements) for the relevant trace gases in this regime. Given the absorption coefficient and employing the Beer-Lambert law, this yields the trace gas density integrated along the light path for the selected species.

~~This is a valid approximation as long as the absorption does not saturate. Typical optical thicknesses of for polluted areas are on the order of up to 10⁻³, so that saturation does not impact observations.~~

~~Usually, the light-path is slanted and features single and multiple scattering on molecules, cloud droplets and aerosols in the atmosphere. The derived quantity is thus called the slant column density (SCD) and is measured in molecules/cm². It can be interpreted as:-~~

$$\text{SCD}_{\text{NO}_2} = \frac{1}{I_{\text{total}}} \sum_i^{\text{observer}} \int_{\text{sun}} \rho_{\text{NO}_2}(s_i) I_i ds_i,$$

~~which averages the integrated concentration $\rho_{\text{NO}_2}(s_i)$ along all lightpaths s_i (from the sun to the observer) with the respective contribution I_i of this light path to the total intensity I_{total} observed at the instrument ($I_{\text{total}} = \sum_i I_i$). More details on the DOAS analysis can be found in ? and references therein.~~

For this study, we use data from the Bremen GOME-2 slant column density product as described by ? and ?, which includes an NO₂ fit in the wavelength range from 425–497 nm. We analyze data from 4 January 2007 to 31 December 2011. ~~In order to improve spatial resolution and to reduce the effects of photochemistry on NO₂, backscan-pixels, ascending node pixels and pixels with a solar zenith angle of sza > 80° were excluded from the data.~~

~~For most purposes~~ ~~In most previous work~~, our GOME-2 NO₂ product uses FRESKO+ (??) to determine the cloud fraction and excludes pixels with a cloud fraction of CF ≥ 0.2. ~~For~~ ~~However~~, for the analysis of NO₂ long-range transport, no cloud-filtering was applied to the data, ~~as opposed to common practice~~. A systematic study of this phenomenon requires us to include cloudy data in the study, as ~~most many~~ transport events are associated with frontal systems which

are accompanied by clouds and these events would otherwise only be partly visible or entirely missing in the data.

After the trace gas retrieval we have obtained a 2-dimensional map of the global slant column density as it is observed over the Earth's surface, for each day. However, the slant column density alone is hard to interpret. Therefore, we convert the slant column density to the vertical column density (VCD), which is independent of the light path and is a measure of the trace gas concentration integrated vertically from the surface of the Earth to the top of the atmosphere (ToA):

$$\text{VCD}_{\text{NO}_2} = \int_{\text{surface}}^{\text{ToA}} \rho_{\text{NO}_2}(h) dh.$$

In this study, we are interested in the tropospheric NO₂ distribution only, so we apply a stratospheric correction, removing any stratospheric contributions. Here, the stratospheric part of the measured NO₂ column is estimated from a 3-D chemical transport model (CTM), the B3dCTM (?). The obtained stratospheric NO₂ is offset to represent the zonally averaged NO₂ in the reference sector (?): a strip over the remote Pacific – between 180°W and 140°W – which is assumed to not contain any tropospheric NO₂. This is then converted to a stratospheric slant column density map (via a stratospheric air-mass factor, see below) and subsequently subtracted from the total slant column density map to produce the tropospheric slant column density map.

This value contains no information about the altitude of the measured trace gas. To estimate the NO₂ pollution in a pixel, we need to model the lightpath and apply a corresponding correction – called the air-mass factor (AMF) – to obtain the vertical column density.

$$\text{VCD} = \frac{\text{SCD}}{\text{AMF}} \quad (1)$$

The air-mass factor for a scene is derived from radiative transfer models initialized with a suitable scenario.

As typical NO₂ long-range transport events extend over hundreds of kilometers, we grid the retrieved data onto a grid with a cell size of 0.5° × 0.5° – to speed up computing times and reduce retrieval uncertainties – without significantly impacting our results.

2.1 Vertical column densities (VCDs) in partially cloudy scenes

To convert the NO₂ slant-column densities into vertical-column densities, we need to determine the air-mass factor, which interrelates these two. The air-mass factor describes, by which factor the vertical column density differs from the slant column density due to the radiative transfer (RT) from light source to observer.

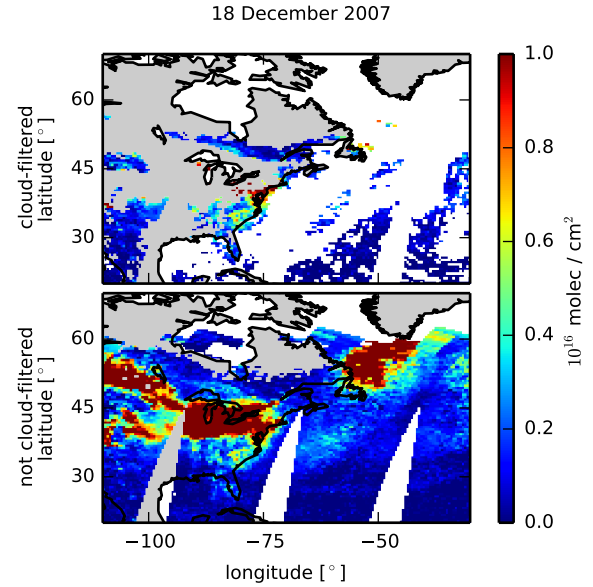


Fig. 1. GOME-2 tropospheric NO₂ vertical column density with (top) cloud-filtering enabled (FRESCO+ cloud fraction > 20%) and (bottom) disabled on 18 December 2007. A plume associated to a long-range transport event (following a cyclone) can be seen south of Greenland only in the non-filtered data.

We refrain from using a cloud-filter which removes satellite observations that show a certain degree of cloudiness. Long-range transport events are commonly linked to frontal systems and thus to cloud formation. In order to observe these events, we need to take cloudy pixels into account (see Fig. 1).

For cloud-free scenes, usually a climatology of vertical profiles is used to determine the air-mass factor under various geometric configurations via radiative transfer simulations. Here the computation of air-mass factor, we use the SCI-ATRAN 3.1 radiative transfer model (?) to perform air-mass factor calculations.

For cloudy scenes this approach is not sufficient. The cloud drastically impacts the radiative transfer and may have varying influence on the air-mass factor, depending on the relation between the vertical profile of the and the cloud. Especially, the so-called block air-mass factor calculate altitude dependent block air-mass factors (BAMF) is altered. The block air-mass factor denotes the sensitivity of the observations to a trace gas at a given altitude (?). It can be visualized as the mean factor of light-path enhancement at a specific altitude. Neglecting saturation effects, the block air-mass factor relates to the air-mass factor as:

$$\text{AMF} = \frac{\int_{\text{surface}}^{\text{ToA}} \text{BAMF}(h) \rho(h) dh}{\int_{\text{surface}}^{\text{ToA}} \rho(h) dh} \quad (2)$$

Clouds alter the block air-mass factor in multiple ways. The exact behavior depends on geometry and cloud properties. Typical effects are ~~(??)~~ ~~(???)~~:

- The cloud provides a surface of high reflectivity. The block air-mass factor is enhanced close over the cloud top (albedo effect).
- Inside the cloud, multiple scattering takes place which elongates the mean light path and leads to a further increased block air-mass factor in the top layers. Less light penetrates into the lower layers, which in turn rapidly decreases the block air-mass factor towards the cloud bottom (multiple scattering effect).
- Little light penetrates to the atmosphere below the cloud and even less gets transmitted again to the satellite, which leads to a relatively small and stable block air-mass factor for the atmosphere between surface and cloud (shielding effect).

These effects are illustrated in Fig. 2.

Further interesting effects can occur when clouds reside over bright surfaces (snow and ice). Due to the high reflectivity of the surface, not much light is absorbed there. Instead, light between the surface and the cloud bottom will continually propagate back and forth until it finally penetrates the cloud and reaches the instrument. This leads to a vastly increased light-path and can lead to an increased block air-mass factor below the cloud due to the cloud's presence.

This effect is hard to find in satellite data, as typical observation geometries over bright scenes allow only for a mitigation of the shielding effect, not an absolute enhancement of the air-mass factor. It may, however, lead to an overestimation of NO₂ content when plumes are observed over sea-ice.

To take the effect of clouds on the radiative transfer into account, we first divide each satellite pixel into a cloudy and a cloud-free fraction, thus obtaining a geometric cloud fraction (CF). We obtain this cloud fraction by modeling the reflectivity of the pixel both under clear conditions and under cloudy conditions (with assumed cloud properties). The reflectivity R is derived from nadir measurements and solar irradiance as-

$$R(437.5 \text{ nm}) = \frac{I_{\text{nadir}}(437.5 \text{ nm})}{I_0(437.5 \text{ nm})}.$$

at 437.5 nm

Then, the cloud fraction is obtained by modelling the observed reflectivity from the combined reflectivity of cloudy and clear part, similar to the method described in ?, but using directly the wavelength range in which we retrieve NO₂ optical depths.

$$CF = \frac{R_{\text{obs}} - R_{\text{cloud-free}}}{R_{\text{cloudy}} - R_{\text{cloud-free}}} \quad (3)$$

This is a simple approach. It is quick and robust and operates directly in the wavelength we are interested in, 437.5 nm, where the most relevant absorption features are located. ~~For this study~~ It is thus representative of the impact clouds have on the retrieval of NO₂ for this study. There are many other cloud retrievals operating on GOME-2 data, none of which operate on the spectral band used for retrieval of NO₂. A comparison to FRESKO+ cloud fractions shows that overall, the results of both cloud retrievals are very similar with a narrow band of scattering. Over bright surfaces and sunglint, larger deviations are possible.

Here, we use the monthly albedo climatologies based on MERIS data by ? to model cloudy and cloud-free reflectivities. Operationally, we obtain the reflectivity values from a look-up table.

However, this yields only the geometric cloud fraction. For purposes of determining the air-mass factor, we need to use the radiance cloud fraction: the fraction of the radiation entering the detector that was influenced by clouds. This is obtained by weighting the cloud fraction with the modeled reflectivities.

$$CF_{\text{radiance}} = \frac{CF R_{\text{cloudy}}}{CF R_{\text{cloudy}} + (1 - CF) R_{\text{cloud-free}}}$$

~~Usually, this value~~ Usually, the cloud radiance fraction will be larger than the geometric cloud fraction, because cloud reflectivities are higher than surface reflectivities for all but very white surfaces with an albedo $\gtrsim 0.8$. This means, that even small cloud fractions have a strong impact on the air-mass factor.

Now Finally, we determine the air-mass factor by weighting the cloudy and cloud-free air-mass factor by the radiance cloud fraction:

$$AMF_{\text{total}} = CF_{\text{radiance}} \cdot AMF_{\text{cloudy}} + (1 - CF_{\text{radiance}}) \cdot AMF_{\text{cloud-free}}. \quad (4)$$

Usually, the cloud-free air-mass factor is determined either from a standard atmospheric profile or from climatological simulations (like MOZART, ?). These cannot, however, be used for analysis of long-range transport events, as the NO₂ will typically be strongly localized in altitude (?) and deviate from stationary conditions.

The air-mass factor depends on where in vertical direction the trace gas is situated. This effect becomes stronger when there are clouds in the scene. However, the precise altitude is not needed, as long as we know the position of the trace gas with respect to the cloud (see Fig. 2 and ?).

Measurements from the TRACE-P campaign (?) suggest that, for a long-range transport event associated with a cold front passing over an emission region, the trace gases (in their case CO) tend to be homogeneously mixed inside the cloud.

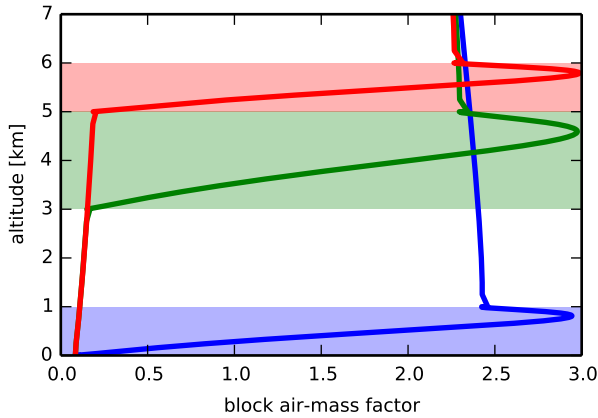


Fig. 2. Three exemplary block air-mass factors ($\lambda = 437.5$ nm) for scenes with clouds of optical thickness 20 at the respective shaded altitudes. Solar zenith angle and viewing angle are set to 0° , the surface albedo is set to $a = 0.1$. The absolute altitudes of trace gas and cloud only have a small impact on sensitivity – the dominant effect stems from the relation of their respective altitudes.

It is possible that fractions of the trace gas content are also situated below or above the cloud due to the nature of convective processes, condensation and subsidence of liquid water droplets. In the absence of coincident in-situ observations of cloud properties and NO₂ profiles, model data can be used to investigate the relative positioning of the two quantities during long-range transport events.

A—We have used MACC-II reanalysis (?) liquid and frozen water content and NO₂ concentrations to find further indications of the relation altitude between clouds and NO₂ for a prominent case of an NO₂ long-range transport event linked to clouds (Fig. 3). For beginning of October 2010 in Europe (detailed case study in Sect. 5.4), we find that profiles at three locations of the plume, corresponding to different plume ages, profiles of NO₂ concentrations and liquid and frozen water content are very similar with a strong overlap of high-content altitude ranges (Fig. 4).

This is a strong indication that at least in this occasion, our assumptions are justified and the modeled air-mass factor is roughly representative of the actual air-mass factor of our observations. However, this is only anecdotal evidence. We could not devise a simple way to systematically test our assumption on a large population of long-range transport plumes, as plumes found in GOME-2 data have to be identified by hand in the model data and an objective comparison of vertical distributions is not a straight forward task.

Even though the results shown in Fig. 4 match our expectations, profiles of elevated NO₂ in model data have to be interpreted with caution as they are the result of parameterized convection which may not be adequate for

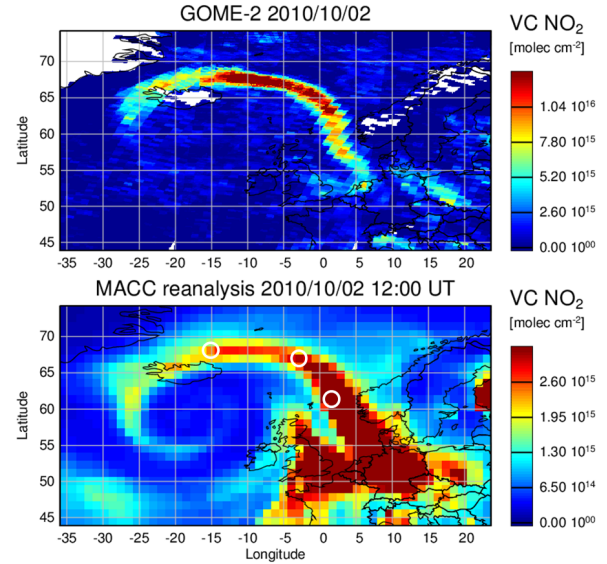


Fig. 3. Comparison of the NO₂ long-range transport plume near Europe on 02 October 2010 in GOME-2 and MACC-II reanalysis data. Note the difference in colorscale. White circles indicate the locations at which vertical profiles of NO₂ and water content were determined. The export is clearly visible in both satellite and model data. However, the model data show significantly lower NO₂ concentrations.

all lifting scenarios and can introduce artifacts, e.g. when the maximum altitude is capped. Clouds in CTMs are devised from different parameterizations, and the relation of cloud and NO₂ altitude will depend on the details of the parameterizations used. While the model data examples shown support our approach, this aspect needs to be further investigated in the future, preferably with in-situ observations from aircrafts.

To quantify the uncertainties introduced by our assumptions, we performed a detailed analysis of the air-mass factor's dependency on radiation geometry and surface properties for varying relative cloud and NO₂ profiles. This analysis shows that if the NO₂ is well mixed inside the cloud, the errors of missing NO₂ slightly above or below the cloud are on the order of $\Delta\text{AMF}/\text{AMF} \lesssim 15\%$ (Fig. 5). This simplification holds, if most of the NO₂ is mixed inside the cloud.

If significant parts of the trace gas are situated above (or below) the cloud, we will underestimate (respectively overestimate) the air-mass factor. This effect is especially strong under non-nadir viewing and irradiation geometries. However, the effects of missing NO₂ above and below the cloud compensate each other for solar zenith angles of $40\text{--}70^\circ$, which is the range most relevant for NO₂ long-range transport.

Based on these sensitivity studies, an NO₂ block profile that is homogeneously mixed inside the cloud and zero

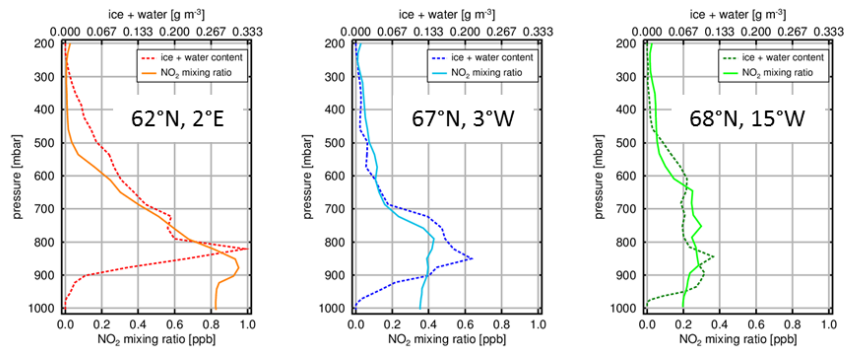


Fig. 4. Comparison of NO₂ mixing ratio and frozen and liquid water content from MACC-II reanalysis data for three locations (roughly corresponding to increasing plume age from left to right) in the plume shown in Fig. 3. The distributions are highly correlated, indicating that our assumptions of full mixing of NO₂ within a present cloud is justified.

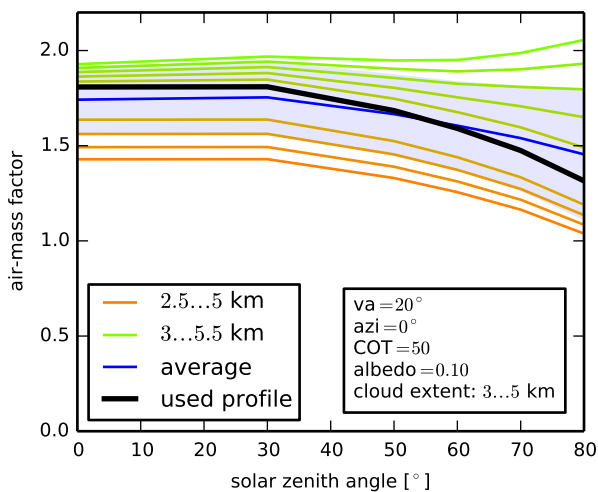


Fig. 5. Illustration of the air-mass factor dependency on the solar zenith angle for varying NO₂ profiles and an invariant cloud profile. The black line shows the profile used for this study. The ensemble average and the standard deviation are indicated in blue. We used a cloud vertical extent of 3...5 km, a surface albedo $a = 0.1$, a viewing angle $va = 20^\circ$, relative azimuth angle $azi = 0^\circ$ (forward direction) and cloud optical thickness $COT = 50$ (as used for data analysis).

elsewhere is selected as the modeling hypothesis for **cloudy air-mass factors**.

We assume a vertical block profile of both for the cloudy and the clear sky case, where both cloudy and clear sky air-mass factors. More specifically, we assume NO₂ is to be homogeneously distributed between 3–5 km a.g.l. and absent in all other parts of the atmosphere. If present, a cloud is assumed to extend the cloud is modelled as extending over exactly the same altitude range. This approach is used for

simplification and is only valid for long-range transport processes. During such processes, the exact altitude of the NO₂ content has little impact on the resulting air-mass factor as long as any NO₂ will be mixed inside a cloud, if present.

This leads to an inappropriate air-mass factor for regions with NO₂ close to the surface. Since long-range transport events will usually have elevated plumes of NO₂ and this study focusses only on NO₂ over the oceans, no regions with significant amounts of surface NO₂ will enter our further analysis. Thus, we effectively use this air-mass factor only for NO₂ long-range transport events.

A sensitivity study shows that from a broad sample of setups of surface and cloud properties, the 3–5 km a.g.l. scenario is situated right in the center of the resulting air-mass factors (deviating by less than 1% from the mean) over all occurring geometries (Fig. 8). The relative standard deviation of the resulting air-mass factors from the whole set of setups is less than 3% over all viewing geometries.

The estimated tropospheric NO₂ vertical column density (VCD) is finally calculated by applying the combined cloudy and cloud-free air-mass factor to the tropospheric NO₂ slant column density.

The NO₂ product described here is used only for long-range transport analyses over the open ocean, where no concentrated NO₂ emissions take place.

3 Methodology

To detect long-range transport events in a global dataset spanning five years of observation, we implemented an algorithm to find, verify and assess plumes from long-range transport events.

3.1 Identification of potential long-range transport events

As a result of the short lifetime of NO₂ in the planetary boundary layer, observations from satellite show NO₂ to be strongly correlated to emission regions (?????). Long-time averages indicate emission and major outflow regions. NO₂ long-range transport events are isolated events that deviate from steady background pollution. During such an event plumes of NO₂ suddenly appear in the data and – if they persist long enough and observation conditions are favorable – move between subsequent observations.

Analysis of NO₂ long-range transport can be performed by just browsing through the data. For a more thorough and objective analysis, we need to enable computers to systematically find such events.

We therefore have ~~developeped~~ ~~developed~~ an algorithm to identify intercontinental long-range transport events in maps of NO₂ vertical column densities. This algorithm builds on the following premises:

- long-range transport events are suddenly appearing and disappearing anomalies in the daily, global NO₂ observations
- long-range transport events show extended NO₂ plumes which are composed of at least two pixels of $0.5^\circ \times 0.5^\circ$
- long-range transport events can be traced back to source regions with lagrangian transport models

To ensure that we recognize sudden features in the global timeseries, we compute a sliding mean and standard deviation for each day, which includes a number n_{days} of observations before and after the day in question. We do not include the day itself to avoid self-referencing of the plume.

For all further analysis, we only consider measurements over the oceans and mask out continental data. The oceans with their low NO_x sources allow us to see plumes clearly, whereas we might easily miss them over the continents or interpret varying emissions or effects of meteorological conditions on NO₂ observations as long-range transport events. Plumes over the ocean can only result from transport processes ~~or stem~~, from artifacts in the observations or retrieval ~~or from individual events such as large thunderstorms and or uncontrolled fires on oil platforms~~. NO_x emissions from lightning are rarely detected in satellite data, due to both small vertical column densities and unfavorable viewing conditions (?). ~~However, in some cases they can interfere with our retrieval as discussed in section Sect. 4.4.~~ Emissions from both ships and aircraft are too ~~diluted and too frequent~~ regular and too small in absolute concentrations to appear as anomalous plumes in the data.

For each day, we select those pixels, which show NO₂ columns at least $n_{\text{seed}} \times \sigma$ above the mean. These are the candidate pixels. All candidate pixels within a great-circle

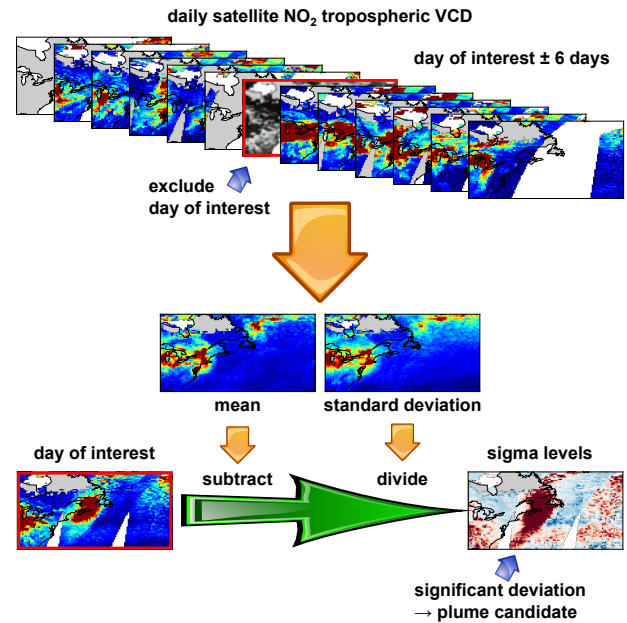


Fig. 6. Schematics of how GOME-2 satellite data is prepared in order to detect NO₂ long-range transport plumes are detected using our algorithm events. The observational data are compared to a sliding mean and standard deviation of the six days preceding and following the day of observation. Strong positive anomalies in NO₂ vertical column densities are selected as potential for long-range transport plumes.

distance $\Delta\theta$ of another pixel become seeds. All seeds within a distance of $\Delta\theta$ are merged. Pixels that have no neighbor within $\Delta\theta$ are discarded as outliers. The algorithm preparation of GOME-2 data is illustrated in Fig. 6. The further processing of these data to detect, assess and verify plumes is shown in Fig. 7.

These seeds – containing two or more pixels – are now grown: all adjacent pixels which are at least $n_{\text{member}}\sigma$ above the mean are merged into the seed to form the plume. We iterate this process until no further pixels match the criteria. We discard all plumes that include less than $n_{\text{min,molec}}$ molecules of NO₂ for computational purposes and to filter out false positives from noise in the data.

For our analysis, we chose the following constants: $n_{\text{days}} = \pm 6$, $n_{\text{seed}} = 3$, $n_{\text{member}} = 2$, $\Delta\theta = 1.0^\circ$, and $n_{\text{min,molec}} = 5 \times 10^{30}$ molecules.

3.2 Backtracking of potential long-range transport events

Long-range transport events are dynamic processes. We perform backtracking of the plumes identified in the previous step. Then, we assess the properties of the plumes – in particular their altitude and origin – and discriminate between

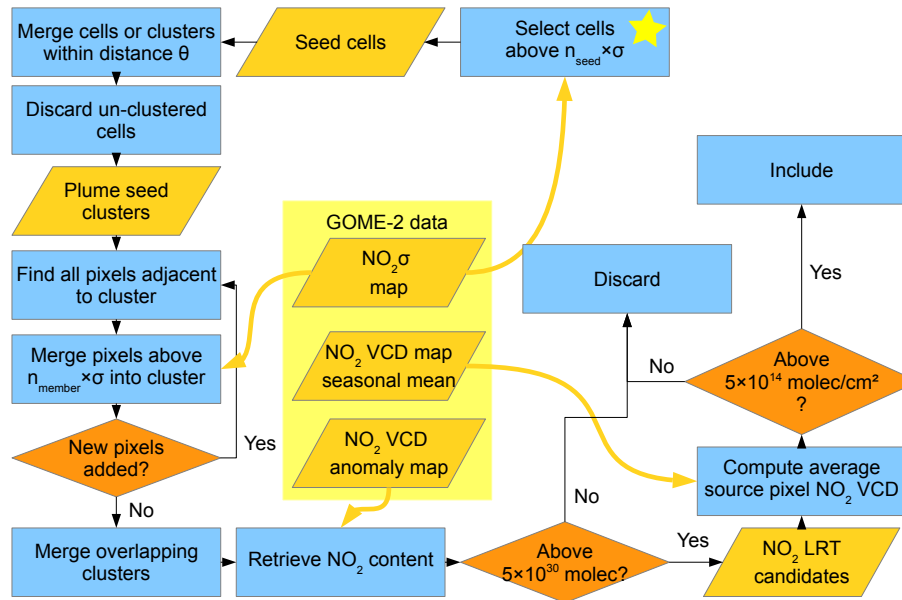


Fig. 7. Schematics of how long-range transport plumes are detected using our algorithm, starting from the prepared GOME-2 data as shown in Fig. 6.

615 actual long-range transport events and artifacts from incom- 645
 620 plete removal of stratospheric NO₂, the GOME-2 instrument
 625 instrument noise, or diurnal variation.

We employ the HYSPLIT_v4 lagrangian transport model
 630 (???) (???) and supply it with Global Data Assimilation Sys-
 635 tem (GDAS) (?) meteorological-meteorological data as input. For each plume, coordinates of all the associated pix-
 640 els are inserted into HYSPLIT as starting points of back-
 645 trajectories. We do this at multiple altitude levels as we do
 650 not have any altitude information on the NO₂ itself from
 655 the observations. FRESCO+ cloud top height (CTH) can be
 used to verify our assumptions about the vertical relationship
 between NO₂ and cloud, but we chose not to use it for
 determining the altitude of the NO₂, so that a potentially
 incorrect assumption in the air-mass factor calculation does
 not lead to an exclusion of the real backtrajectory.

We select altitudes from 1000m to 6000m in steps of
 500m. HYSPLIT is then run backwards for 120 hours – a lit-
 635 tle more than the reported NO₂ lifetime of up to four-several
 640 days in the free troposphere (?) – and all the snapshots of the
 645 plumes (all associated points at 120 time steps and 11 altitude
 650 levels) are recorded.

For each of these snapshots we retrieve the seasonal mean
 635 tropospheric NO₂ vertical column density for each point
 640 that is within the planetary boundary layer (assumed to
 645 reach up to 1000m). We obtain these values from the sea-
 650 sonally averaged cloud-free GOME-2 data from 2007 to
 655 2011, gridded to the same resolution as the data used for
 plume retrieval. Pixels in the seasonal average that are hit by
 multiple backtrajectories are included multiple times, leading

to a weighting of sources. A value of zero is recorded for
 points above the boundary layer. These values serve as a
 measure of the pollution which is available for transport at
 this point of the backtrajectory.

We compute a simple score for each snapshot to select the
 most likely source of the plume. This score implicitly favors
 a low dispersion of the points and thus also a young plume.
 It is computed as the number of trajectories that reside in the
 continental planetary boundary layer (below 1000ma.s.l.)
 for every time step in the backtrajectory (snapshot).

We select the snapshot with the highest score to mark the
 beginning of the transport event and discard all snapshots
 from other altitudes and from all timesteps that go further
 back in time, leaving us only with the preferred trajectory.

As we derive both the altitude of the plume and the
 origin from this analysis, there may be ambiguities in the
 results. Backtrajectories from multiple altitudes may lead
 to the same or different source regions. While this is rather
 uncommon, when inspecting results, it may affect parts of
 the results. Also, it is possible that occasional NO₂ plumes
 that do not belong to a long-range transport event are falsely
 assigned a backtrajectory to a source region. We do not have
 a way to discriminate between these cases. However, we have
 inspected backtrajectories of randomly selected events from
 our results and most backtrajectories are plausible.

3.3 Verification of potential long-range transport events

After we have determined the most likely trajectory, we as-
 635 sess whether or not this is actually a long-range transport

event. We sum up the average seasonal clear-sky NO₂ vertical column density at the beginning of the trajectory of each pixel in the plume. The ratio between this measure of NO₂ pollution in the determined source region and the number of pixels in the plume has to exceed a minimum value in order to verify this plume as belonging to a long-range transport event. Effectively, this determines the average source region NO₂ vertical column density for this plume.

We demand that the ~~average~~-source region pollution averaged over all pixels in the plume exceeds 5×10^{14} molecules/cm² for a credible long-range transport event. This criterion is based on manual fine-tuning to find an optimum balance between obvious false positive and false negative events, by browsing through the results. All plumes that do not fulfill this criterion are discarded. Roughly 56% of all plumes are discarded by this criterion.

This method is feasible because we analyze plumes only over the ocean and assume that all source regions are located on the continents. While emissions from ships, airplanes and lightning contribute to the overall NO₂ budget, they are associated with significantly lower NO₂ vertical column densities than continental emissions, with an observed NO₂ vertical column density on the order of 10^{15} molecules/cm² for the most polluted shipping lanes (?). Due to stray pixels in the backtrajectories and the large spatial extent of NO₂ long-range transport events, this local concentration is not enough to qualify shipping lanes as origin of long-range transport by the above criterion, due to the averaging process.

3.4 Assessment of properties

The aforementioned method allows us not only to identify transport-related NO₂ plumes but also to derive a number of properties for each individual long-range transport event. These properties include:

- the total area encompassed by the plume (from the extent of the pixels)
- the NO₂ content in each pixel (excess tropospheric NO₂ vertical column density above the sliding mean)
- the total NO₂ content in units of molecules or mass in GgN (by summing up vertical columns over the plume area)
- the source region of the plume
- the age of the plume since it left the boundary layer
- the altitude evolution of the plume from emission to observation
- the horizontal velocity of the plume

In some cases, it is possible to identify the same plume at earlier or later time steps in the satellite data to get a more

detailed analysis of such an event. Currently, we need to do this manually and therefore limit this part of the analysis to selected case studies.

4 Limitations

To apply the method outlined in the previous section, we have to limit the analysis to favorable conditions and assume simple long-range transport scenarios. There are a number of factors which contribute to the overall uncertainty of our developed method.

4.1 Satellite data

NO₂ observations from satellite are prone to retrieval errors, when trace gas absorption cross sections are fitted to the spectral radiance to retrieve the slant column density. With regard to the fit residual, we estimate the errors for an individual pixel to be on the order of $5 \cdot 10^{14}$ molecules/cm² in equatorial regions, which amounts to up to a few percent. Plumes have to exceed an NO₂ content of 5×10^{30} molecules to be included in our study, which typically amounts to tens or hundreds of polluted pixels. This, together with the regridding of the data, partially mitigates the uncertainties.

The GOME-2 instruments measure only in daylight and cannot observe NO₂ during winter at ~~high~~-higher latitudes. This impedes the analysis of long-range transport events traveling to the Arctic, one of the most sensitive areas of interest for the long-range transport of air pollution (?).

4.2 Air-mass factors

To obtain NO₂ vertical column densities, we assume a profile that locates NO₂ between 3–5 km in altitude. Sensitivity studies show that the results for the NO₂ air-mass factor do not vary strongly within this altitude range (Fig. 8) if it is well mixed within the cloud or elevated from the surface in the absence of a cloud. The standard deviation of air-mass factors for 2 km thick layers of NO₂ mixed inside clouds for different altitudes is on the order of 3% for typical observation geometries. Variations of the thickness of the cloud and NO₂ layer have a similarly small effect.

Based on ?, we assume that the trace gas will be homogeneously mixed inside any cloud that may be present and stretch over an altitude range of 3–5 km during a long-range transport event. Our sensitivity studies show (Fig. 5) that the air-mass factor displays only small variance when a fraction of the trace gas is present above or below the cloud, as long as the majority is mixed inside the cloud. For this study, we chose the assumptions such that they produce the values near the center of the air-mass factors of all plausible NO₂-cloud-distributions.

Due to the lack of reliable information on the cloud profile (cloud retrievals typically only yield the cloud top and bottom heights), we use a homogeneous profile. We do not

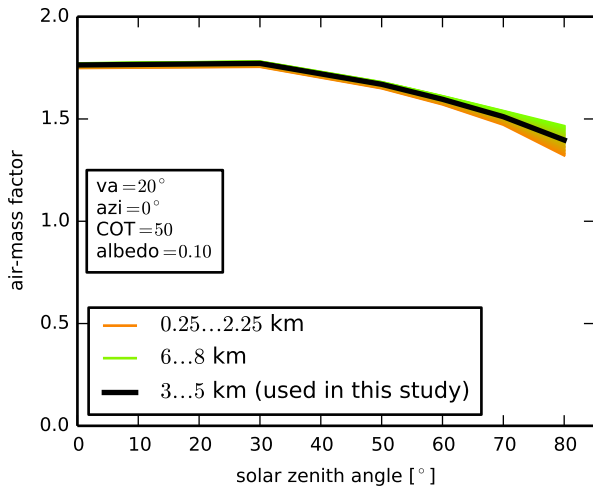


Fig. 8. Sample air-mass factor dependency on solar zenith angle for NO₂ fully mixed inside clouds at varying altitudes. The black line indicates the cloud and NO₂ profile used in this study. We used a surface albedo $a = 0.1$, a viewing angle $va = 20^\circ$, relative azimuth angle $azi = 0^\circ$ (forward direction) and cloud optical thickness $COT = 50$ (as was used for data analysis).

Sensitivity studies show that the results are relatively stable with regards to these parameters. The used parameter sets were chosen to allow deriving a good result in reasonable computation time. Increasing the minimum distance between two distinct plumes will lead to slightly more plumes with high masses.

After plumes are retrieved, varying selection criteria for the preferred backtrajectory and varying verification criteria for the plume will lead to slightly different results. We have therefore implemented criteria that are as simple as possible while producing results that are consistent with manual inspection of a range of sample plumes.

The Lagrangian transport simulations we perform for each plume are also affected by uncertainties. Due to the coarse resolution of the used meteorological and NO₂ data – both vertically and horizontally – individual pixels will eventually diverge from the bulk in case of chaotic movement under conditions with strong winds. This is especially true for old plumes which provide the least reliable data. In most cases the bulk of the plume will stay relatively close together along the backtrajectory, so that stray pixels are not a problem.

Occasionally, a sudden emission of NO₂ over the ocean may also be classified as long-range transport event by our algorithm, when backtrajectories to a prominent emission region exist. This could only be avoided by cross-referencing events with a catalogue of such oceanic emission events.

We do not take plumes over the continents into account. There, fluctuating sources, albedo and topography make the analysis of continental long-range transport challenging. When we limit the analysis to the ocean, we have a data set that is much easier to interpret. However, we are prone to losing parts of plumes which are just on the shore. We also do not detect any continental plumes which do not move onto the ocean.

4.4 Lightning NO_x

There is another source of NO₂ over the ocean: lightning (?). ? report that approximately $5 \pm 3 \text{ TgN/a}$ may originate from NO_x emitted by lightning (LiNO_x). ? show that NO_x concentrations in thunderstorm clouds may be higher than 10 ppbv. They also show that only a small fraction of this LiNO_x is located in the cloud top, where the sensitivity of satellite observations is high. Instead, most of it is located in the lower parts of the cloud or below the cloud, where the sensitivity of satellite observations is low.

For this study we tried to locate major plumes of LiNO_x found in MOZAIC data (?). Only a very small fraction of these events was found in corresponding SCIAMACHY NO₂ satellite data, which was processed in the same way as the GOME-2 data in this study.

Additionally, the verification using backtrajectories makes it unlikely that LiNO_x plumes are classified as long-range transport events in this study. ? report that in their NO₂ long-range transport study, LiNO_x

take the effects of aerosols explicitly into account, as long-range transport plumes tend to travel at elevated altitudes. This eliminates the effects of sea-spray. The effects of other aerosols should partially be mitigated by our cloud product. The remaining effect should be on the order of less than a few percent.

We do not take into account multi-layered clouds. In most cases, these would reduce the NO₂ signal and leave the plume or parts of it undetected by our algorithm. If NO₂ mixed inside a cloud would reside above another cloud, this could lead to an overestimation of NO₂ vertical column density due to an elongated light-path. This is not likely as most plumes tend to reside at relatively low altitudes.

4.3 Plume retrieval

The results of the long-range transport plume retrieval algorithm depend on its input parameters. The chosen thresholds and averaging windows are a result of manual inspection of satellite scenes and comparison to the results from the retrieval.

There are several parameters of interest:

- the σ -levels chosen for seed pixels and member pixels of a plume
- the time frame for the sliding mean calculations
- the maximum distance at which plumes are merged (i.e. the minimum distance of two distinct plumes)

is likely to contribute to the total NO₂ content, but is most likely not the only or dominant source.

850 However, low-pressure regions – which turn out to foster long-range transport – are often linked to thunderstorms which will produce LiNO_x, thereby creating a higher 900 probability of lightning NO₂ contamination of our data. As there is no way to unambiguously distinguish NO₂ from lightning and transport over the ocean in satellite data, this 855 is an additional source of uncertainty in our estimates.

5 Case studies

To illustrate the nature of NO₂ long-range transport events and the successful application of the detection algorithm, we have selected four prominent samples from the collected set of events to scrutinize them in detail.

We use data from the NCEP/NCAR Reanalysis Project (?) to investigate meteorological ~~conditions~~ conditions that accompany detected long-range transport events. Detailed properties of the plumes ~~occurring~~ occurring during long-range transport events (for each observation) are given in Table 1.

5.1 North Atlantic, 17–19 December 2007

Fig. 9 shows a striking example of an NO₂ long-range transport event in the western North Atlantic from 17 to 19 December 2007. Unfortunately, GOME-2 was operated in narrow-swath mode on 16 December 2007, so that we cannot observe how the plume separates from its emission region while being uplifted during the course of this day.

875 The NO₂ plume originates from the East Coast of North America, near the major emission regions of New York, Boston and Chicago. It closely follows the center of a rapidly developing low-pressure system crossing the region from south-west to north-east. After two days, it crosses Newfoundland and subsequently disappears near Greenland in the Arctic night where GOME-2 cannot observe NO₂ vertical column densities. The origin and transport direction of this NO₂ long-range transport event are typical for this region and lie within the major storm track to the East of North America (?).

This mechanism of NO₂ long-range transport has been analyzed in a case study by ?. Unlike that study, here the NO₂ is centered on the cyclone as seen in NCEP DOE AMIP-II Reanalysis mean sea level pressure data. When we inspect further prominent long-range transport events emitted from the North American East Coast, we find that the NO₂ plumes typically follow a rapidly forming cyclone.

Such clear and long-lasting long-range transport events that can be observed for three consecutive days in GOME-2 data are rare. The reason for that lies in the combination of two phenomena prerequisites for long-range transport,

their typical routes and the specifics of DOAS satellite observations:

- most long-range transport events form in the local winter when because emission rates are high, low pressure systems are common, and NO₂ lifetime is long
- long-range transport events tend to move polewards, if they do not dissolve

This means that many long-lasting plumes will quickly move out of sight of the satellite instrument which cannot observe NO₂ in or near regions of polar night.

From our observations, we estimate the plume to contain roughly 2.31 GgN on the first day of observation. From the backtracing of the long-range transport event, we estimate the plume to be about 50 hours old (since detaching from the planetary boundary layer) at the time of first observation. If we take photochemistry and dilution of the plume in the first 50 hours into account, the amount of nitrogen exported from the continent in this event may have been significantly larger. Unfortunately, the few samples do not allow to estimate even allow to determine a rough estimate of the lifetime of NO₂ in this event.

920 The plume is transported at an altitude between 1.0 km on the first and 2.0 km on the last day of observation, as retrieved from the backtrajectories. FRESKO+ cloud top heights (CTH) for these measurements are derived to lie in the range of 840...650 hPa, corresponding roughly to 1.4...3.5 km. This is consistent with the retrieved altitudes, which do not necessarily denote the top of the NO₂ distribution (and thus the cloud), but the altitude from which most trajectories lead back to a source region which could be assumed to lie in the center of mass of the vertical distribution. The FRESKO+ CTH varies over the extent of the plume by roughly 200 hPa which may indicate that the altitude of the NO₂ is not homogeneous over the plume.

Further properties of the event are summarized in Table 1. We derive the minimum average travel speed of the plume (the actual speed will be higher due to curved trajectories) from these properties, which amounted to 59 km/h from the first to the second observation. On the next day, we can only calculate a lower limit (32 km/h) due to the cut-off at polar night.

Fig. 10 illustrates how closely the trajectory obtained from the backtracing algorithm matches the satellite observations of the plume at earlier times, even though all observations of an NO₂ plume are handled independently. Due to the coarse horizontal, vertical and temporal resolution of the meteorological data, the trajectory is not accurate on the outer rim of the plume; there, trajectories diverge from the main path.

5.2 South Africa, 9–12 July 2008

In the Southern Hemisphere, South Africa is the only region regularly emitting NO₂ long-range transport events. A clear

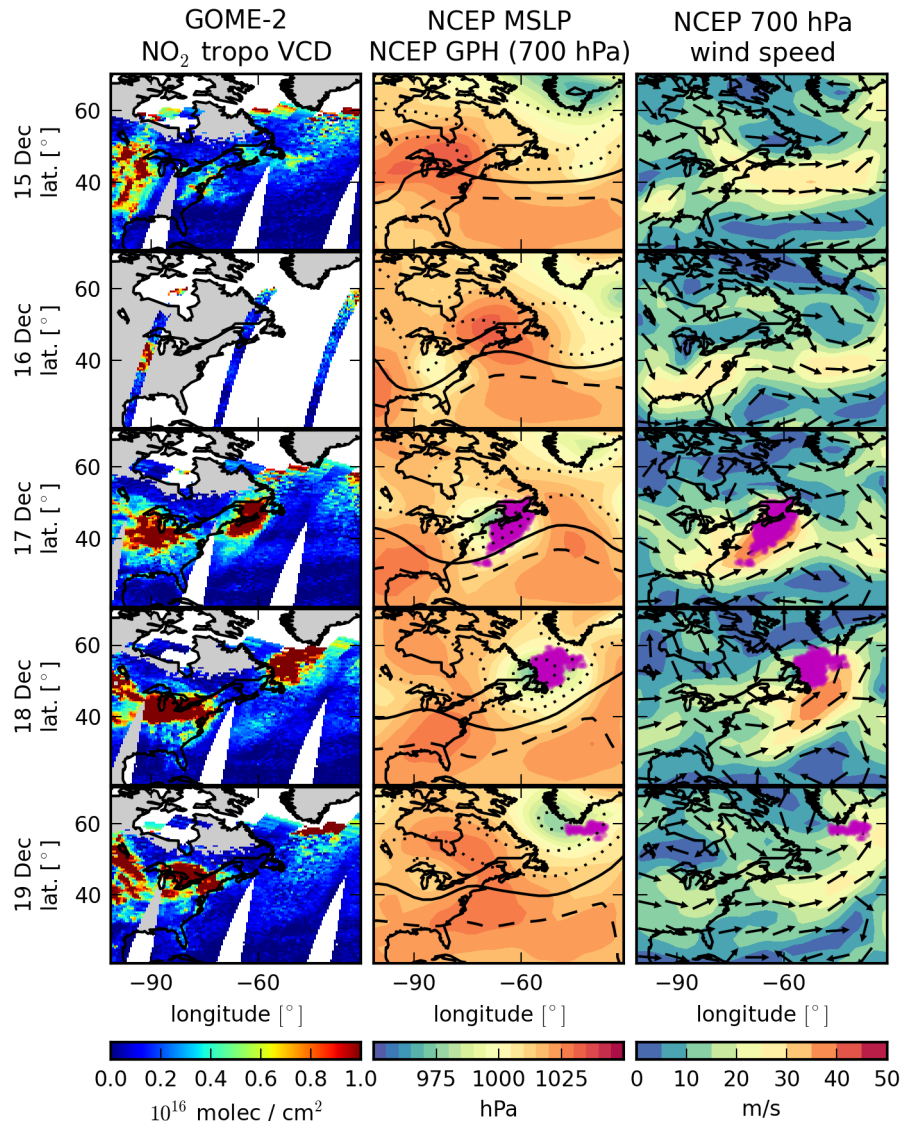


Fig. 9. Timeseries of the days preceding and during a long-range transport event over the North Atlantic on 17 to 19 December 2007. The locations of satellite pixels identified as belonging to the long-range transport plume are indicated by purple circles [in the center and right columns](#). Shown are (left) the GOME-2 NO₂ tropospheric vertical column density, (center) the NCEP DOE AMIP-II Reanalysis mean sea-level pressure (colors) and geopotential height at 700 hPa (contours) and (right) horizontal wind speeds at 700 hPa (amplitude and direction). For geopotential height, the solid line denotes [3km](#), dashed / dotted indicate higher / lower geopotential height in steps of 125 m. A low pressure system is quickly evolving into a cyclone. It elevates an NO₂ plume – as seen in its backtrajectories – and transports it towards Greenland.

event can be seen in the satellite data from 09 July 2008 emitted from the industrial region on the Highveld plateau. It follows the winds in the free troposphere towards the East for several days, disappearing after its last observation on 12 July 2008 near the Australian West Coast (Fig. 11).

South Africa has ideal conditions to create and observe long-range transport events. The Highveld plateau concentrates the nation's industry, injects factory and power plant

exhausts at altitudes of more than 1,500m into the atmosphere, and is an isolated emission region. The prevailing north-westerly winds in this region propel elevated plumes onto the open ocean, which makes it easy to observe them with satellite measurements.

The [World Wide Lightning Location Network \(WWLLN\)](#) finds a significant amount of lightning strikes in the area where the plume is observed on 09 and 10 July 2008

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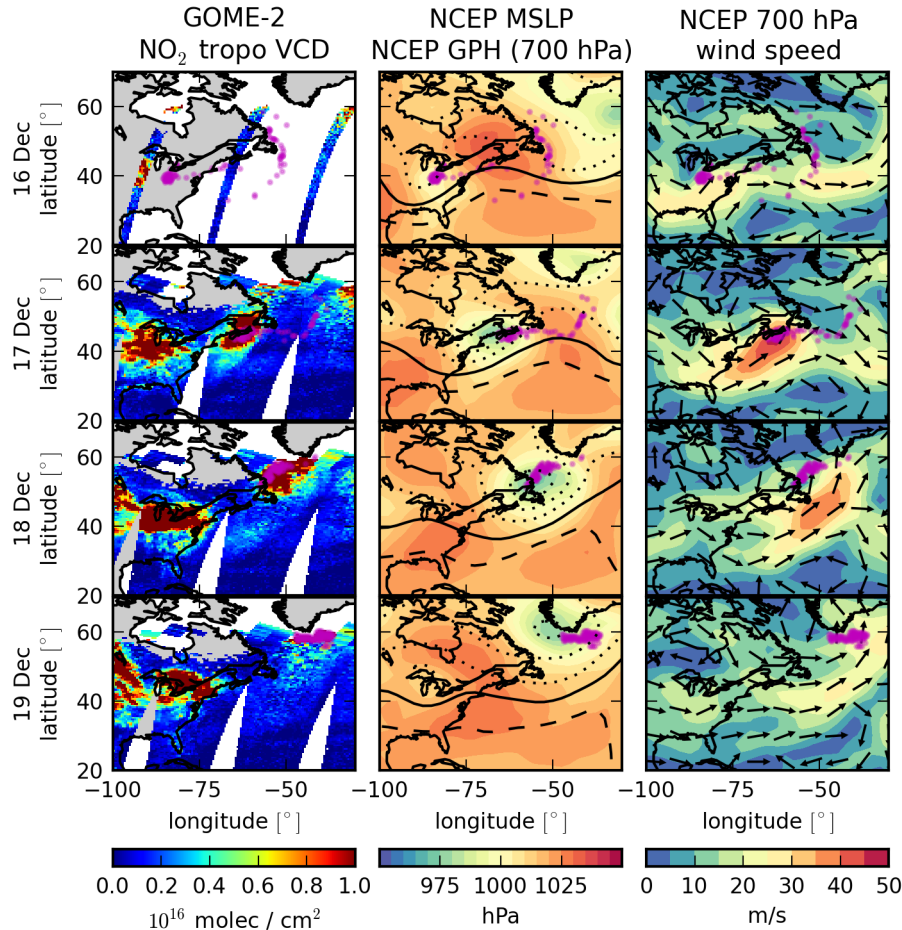


Fig. 10. Illustration of the backtrajectory of the last observation of this long-range transport event (19 December 2007). Data as in Fig. 9, but purple circles indicate the locations of the backtrajectories of the plume from 19 December 2007 at the respective dates. The plume detected on 19 December 2007 is only partially visible due to polar night. This becomes evident when comparing the backtrajectories on earlier dates with the observed NO₂ vertical column densities.

(Fig. 12). On the following days, the – then weaker – thunderstorm and the NO₂ plume are no longer co-located and further impact on the NO₂ plume can be excluded. With our detection algorithm, we cannot distinguish NO₂ from anthropogenic sources and LiNO_x other than by location and trajectory. We cannot tell if this observation actually shows a long-range transport event or LiNO_x or both. It is possible though unlikely, that the observed plume is not anthropogenic in origin, but rather originates in the strong thunderstorm and is then transported further downwind. In that case, it is not clear, why the NO₂ plume and the thunderstorm would separate. It appears more likely that the strong thunderstorm will replenish the NO₂ content of the plume, thereby enhancing its observed lifetime.

It is plausible that long-range transport events will occasionally be accompanied by thunderstorms. These may in turn lead to an enlarged NO₂ content or to an apparent

longer lifetime of NO₂ inside the plume. From our efforts to observe LiNO_x in reported strong thunderstorms and their distinguished seasonal and geographical distribution (Sect. 6.2), however, it appears that thunderstorms will not be the single cause for most of the observed plumes.

This plume bears similarities to the one analyzed by ?. The plume they observed crosses the ocean and arrives at Australia within five days which is consistent with the four consecutive observations in our data. They find thunderstorms with lightning coinciding with the plume on two observations, but the LiNO_x alone could not explain the observed NO₂ vertical column densities in the plume. It might, however, have replenished the plume and thereby increased its apparent lifetime.

The selected long-range transport event is associated to a weak cyclone heading into the Antarctic. A cold front lifts the NO₂ plume up and their trajectories diverge sub-

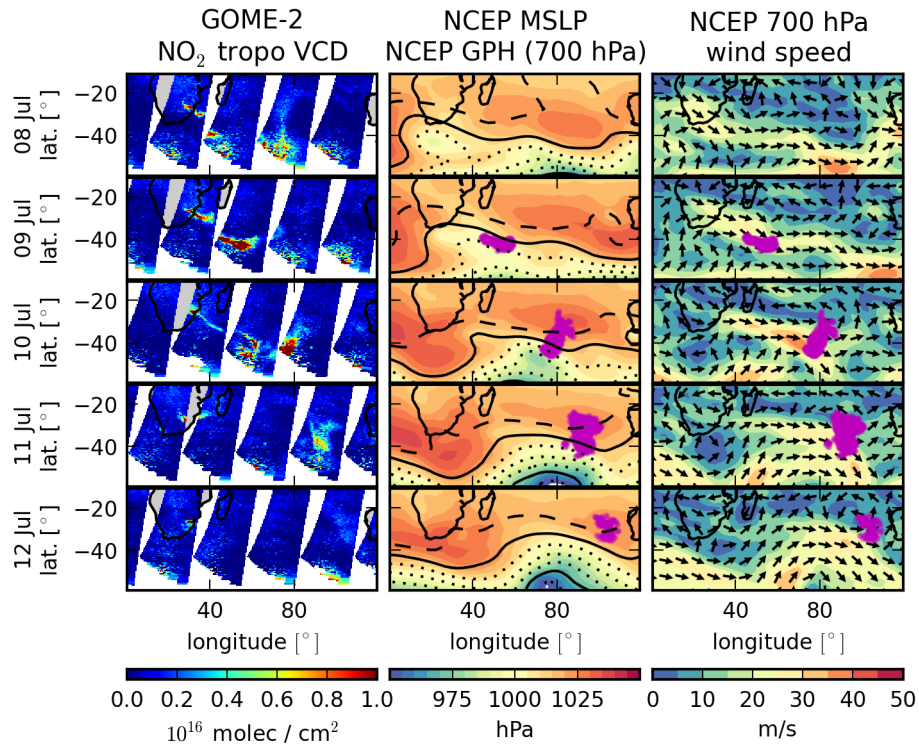


Fig. 11. As for Fig. 9, but showing a long-range transport event emitted from South Africa in July 2008. The NO₂ plume is transported from South Africa to the West Coast of Australia.

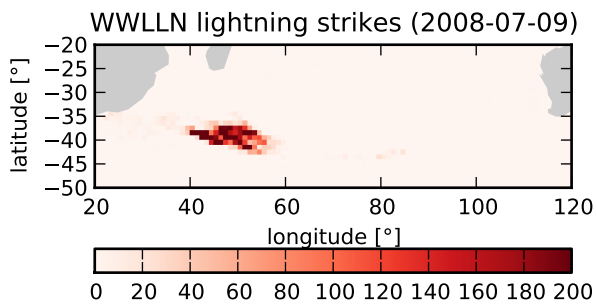


Fig. 12. Number of lightning strikes on 10 July 2008 observed with WWLLN over the ocean near South Africa. The lightning strikes are collocated with the observed position of the NO₂ plume (Fig. 11). Likely, this thunderstorm replenished the NO₂ content of the plume. On the following days, the thunderstorm produces significantly less lightning strikes and is no longer collocated with the transported plume.

sequently. Winds of the free troposphere carry the plume straight to Australia.

1000 We do not observe the plume entering Australia on
 1005 13 July 2008 due to a gap in the data and we do not find any
 traces of it on the following days. Upon arriving on shore
 the NO₂ may have descended and – due to shorter lifetime
 in the planetary boundary layer – dissipated. Also, rain may
 have washed out the NO₂ as HNO₃.

Due to the extent of this event, data gaps cover parts of the
 plume. This could explain why the measured NO₂ content of
 the plume increases from the first to the second day of obser-
 1010 vation. Other mechanisms to increase the observed NO₂
 content are LiNO_x production and conversion of reservoir
 species.

From the first to the second day of observation – while
 the plume follows the cyclone track – the average traveling
 speed is roughly 97 km/h. After the plume and the cyclon
 1015 decouple, the plume only travels at 59 km/h and 51 km/h
 on consecutive days.

~~This plume bears similarities to the one analyzed by ?.
 The plume they observed crosses the ocean and arrives
 at Australia within five days which is consistent with
 the four consecutive observations in our data. They find
 thunderstorms with lightning coinciding with the plume on
 two observations, but the alone cannot explain the observed
 1020 vertical column densities in the plume. It might, however,~~

~~replenish the plume and thereby increase its apparent lifetime.~~

Simulations with FLEXPART (?), a more sophisticated lagrangian transport model, show the plume in their analysis to be traveling at altitudes from 2–6 km a.m.s.l. after it ~~seperated~~ separated from the emission region in the Highveld plateau, which is consistent with our assumptions. In FRESCO+ data, the CTH varies between 750...500 hPa on the 10 July 2008, corresponding roughly to cloud top altitudes of 2.3...5.5 km. This is a bit lower than the estimated plume height of 6 km on this date, but consistent with the following observation. Both indicators point at an elevated plume in the free troposphere.

5.3 Australia, 27–30 April 2008

Australia only emits very few NO₂ plumes due to its limited emission sources, as compared with more populated and more heavily industrialized parts of the globe. However, we find a very long lasting long-range transport event in the data from 27–30 April 2008 which follows stationary wind patterns between a high-pressure system East of New Zealand and a low-pressure system over Antarctica. The plume disperses over the South Pacific ocean between two high-pressure systems (Fig. 13).

The size of this plume suggests that it could be caused by emissions from ~~Australia~~ Australian bush fires. However, MODIS fire count data indicate that there were only few fires in South East and South West Australia. Most strong bush fires were located in North Australia and it is questionable if the short lifetime of the NO₂ in these tropical latitudes would have allowed such a long transport.

Backtrajectories of the event indicate that the NO₂ may originate from the bush fires of both South East and South West Australia. NO₂ and glyoxal (CHOCHO) from large bush fires such as the Black Saturday fires are routinely observed in satellite data (??) and GOME-2 data show elevated NO₂ vertical column densities over southwestern Australia on 25 and 26 April 2008 – on the order of $3 \cdot 10^{15}$ molecules/cm², a factor two higher than background levels. It is likely, that our data product underestimates these values due to a lowered air-mass factor in the presence of black carbon aerosol in bush fire smoke plumes (???). An origin in bush fires would also explain the ~~neccessary~~ necessary lifting of the NO₂ from the planetary boundary layer into the free troposphere in the ~~abscence~~ absence of a frontal system (see ?).

The plume shows an exponential decay in NO₂ content – with a lifetime of approximately 28 hours estimated from observations – even though parts of it are not visible in GOME-2 data. Extrapolating backwards to the time of emission, we estimate the NO₂ content to be about 10.5 GgN. Note, however, that the apparent lifetime of NO₂ in the plume is influenced by conversion to and from reservoir species (especially PAN) which are not observed

in this study and may lead to an increased effective lifetime of NO₂. A detailed analysis of the lifetime of NO₂ in long-range transport events with chemical sinks and sources is beyond the scope of this study and it is not clear if reservoir species will lead to shortened or to a prolonged observed lifetime of NO₂. Besides that, thunderstorms might lead to LiNO_x replenishing the decaying NO₂ content of the plume.

Data from the Lightning Imaging Sensor (LIS, ??) show a small thunderstorm off the coast of Australia on both 27 and 28 April 2008, coinciding with the plume only on 27 April. It appears that the movement of the plume and the thunderstorm are not linked to each other. On 28 April and subsequent days, the plume travels outside the latitude range observed by LIS.

This long-range transport event also shows ~~a deceleration~~ deceleration over time. It starts with a minimum mean velocity of 105 km/h between the first two observations and decelerates to 74 km/h and 56 km/h on the consecutive days. This suggests that the NO₂ plume ~~is stable even when the conditions stays compact even after separating from the meteorological phenomenon~~ leading to its emission ~~diminish~~.

5.4 Central Europe, 1–2 October 2010

Europe is a special case regarding long-range transport events. Due to local wind patterns, the NO₂ plumes are often ejected from the continent towards the north or north-west. Due to topography – strongly emitting regions located near the ocean in a bay – our algorithm retrieves very many long-range transport events here which are often very young at detection time.

On 1 and 2 October 2010 there is a prominent example of a long-range transport event in GOME-2 data. A small but elongated plume of NO₂ is emitted from the BeNeLux and Ruhr area when it is hit by a cyclone. The plume is transported onto the North Sea. It circles around the cyclone and is strongly filamented by the wind shear (see Fig. 14). On 3 October 2010 we can no longer identify the plume in the data. There is an apparent plume of NO₂ between Greenland and Svalbard, where observed NO₂ vertical column densities are highly variable. This anomaly is not detected in the algorithm as it shows no significant deviation above the sliding mean observations and cannot be directly related to a long-range transport event.

The observations suggest that the NO₂ in the plume is transported towards the center of the cyclone. Due to the strong shear winds in the cyclone, the plume is dispersed by 04 October 2010. It was not detected by our algorithm and is hardly discernable in visual inspection of the satellite data.

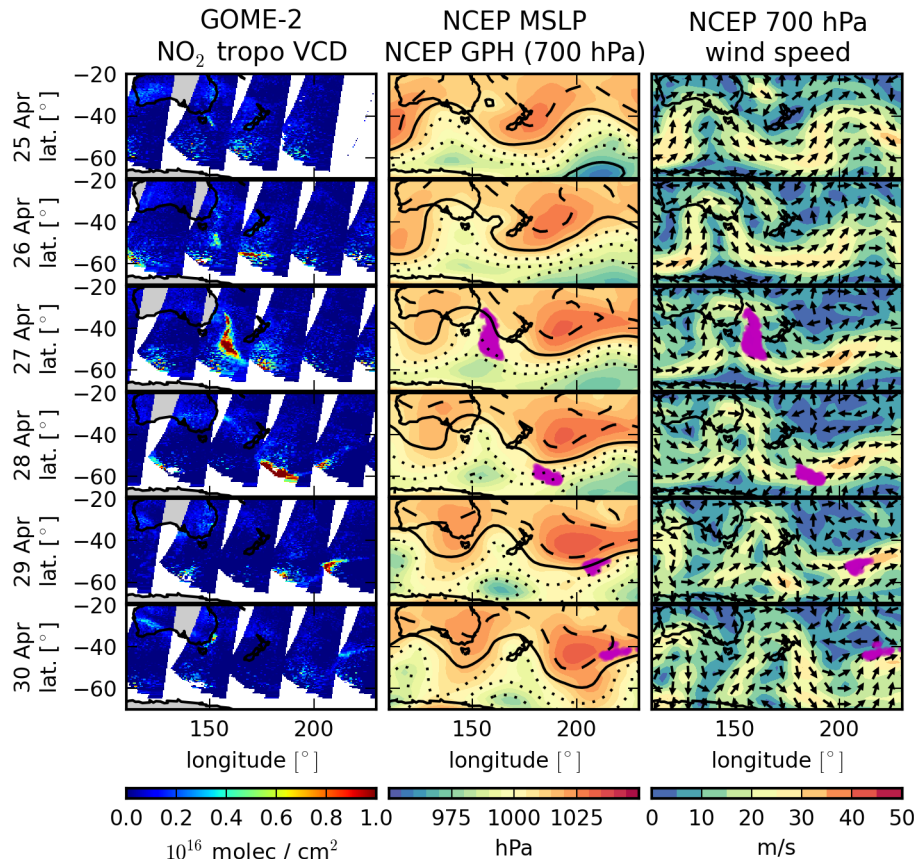


Fig. 13. As for Fig. 9, but showing a long-range transport event emitted in Australia in April 2008. The plume originates most likely from bush fires in Southwest Australia and follows the strong wind currents between highs over the Indian Ocean and lows over the Southern Ocean.

6 Statistical analysis

In the previous section, we described and analyzed well-defined examples of long-range transport events detected by our algorithm which were also found by visual inspection of the data. With the developed algorithm, however, we have the opportunity to analyze a larger dataset and use the automated detection of long-range transport events to perform statistical analyses of this phenomenon over a longer period.

The analysis found a total of 3808 verified NO₂ long-range transport events (out of a total of 8626 events) in the GOME-2 data from 2007 to 2011. Fig. 15 shows their seasonal distribution for Northern and Southern Hemisphere. The distribution shows a strong seasonality in the frequency of long-range transport events; roughly half of all events occur during the local winter quarter. The Northern Hemisphere dominates the statistics due to more high-emission regions at higher latitudes.

We analyze the collection of long-range transport events from our algorithm to gain insight into favoring conditions,

the hotspots and routes, and the range of parameters associated with them. First, we will focus on individual plumes' properties, then on ensemble properties.

6.1 Plume properties

Fig. 16 shows that the NO₂ content of the plumes roughly follows an exponential distribution function:

$$dp(m) = \exp\left(-\frac{m}{m'}\right) dm, \quad (5)$$

where m is the NO₂ content of the plume and m' the scale mass of the distribution. A small scale mass indicates that small plumes dominate the distribution, while a large scale mass indicates that large plumes occur more regularly.

Looking only at the Northern Hemisphere (to exclude counteracting seasonality), we find that $m' = 0.25 \text{ GgN}$ for DJF, $m' = 0.24 \text{ GgN}$ for SON and $m' = 0.16 \text{ GgN}$ for MAM. Due to the low number of plumes, we could not determine m' for JJA. This means that plumes in autumn and

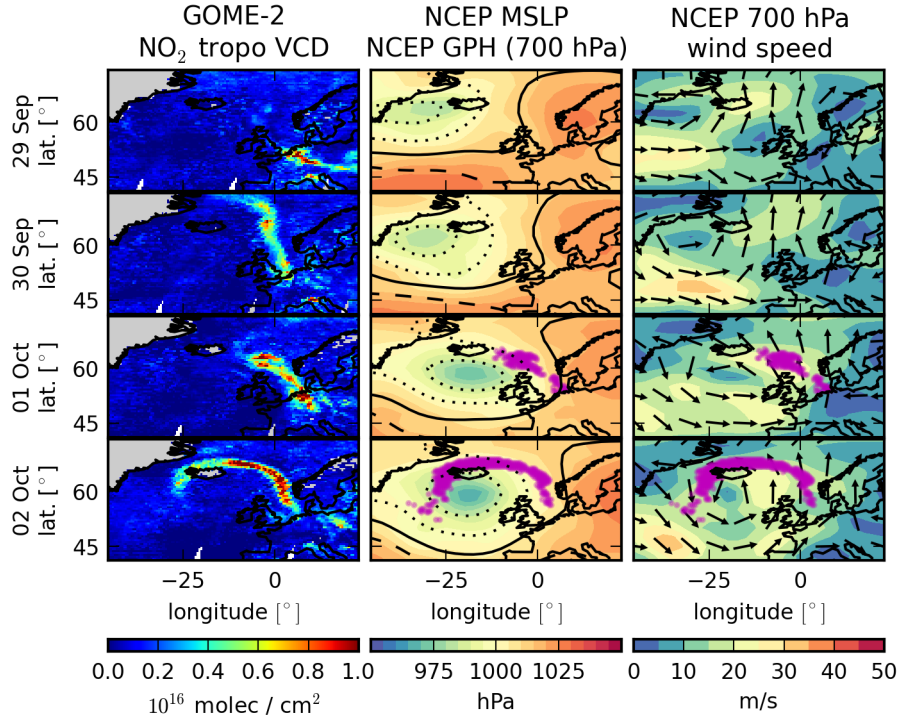


Fig. 14. As for Fig. 9, but showing a long-range transport event emitted in Europe in October 2010. The plume gets highly filamented when entering the cyclone. Note that the plume visible on 30 September 2010 separates from the rest of the plume and appears to have mostly been transported into the Arctic by 01 October 2010. Therefore, we do not include it in our analysis.

Table 1. Properties of NO₂ plumes observed during long-range transport case studies as estimated from GOME-2 data and HYSPLIT backtrajectories. For all plumes, properties (except for plume age) are derived only from the observational data for the given date – no information from prior or later observations is used.

Date	Plume Center		Altitude [km]	Age [h]	NO ₂ content [GgN]	Area [10 ³ km ²]
North Atlantic						
2007-12-17	45° N	63° W	1.0	50	2.31	1093
2007-12-18	55° N	52° W	1.5	73	1.98	698
2007-12-19	58° N	42° W	2.0	95	0.65	207
South Africa						
2008-07-09	42° S	53° E	2.0	50	1.58	642
2008-07-10	41° S	78° E	1.5	73	1.74	1293
2008-07-11	35° S	93° E	6.0	96	1.40	1898
2008-07-12	30° S	103° E	4.5	119	0.39	881
Australia						
2008-04-27	46° S	159° E	4.0	47	1.83	1256
2008-04-28	60° S	175° W	1.0	69	0.89	311
2008-04-29	52° S	152° W	1.5	92	0.45	288
2008-04-30	43° S	141° W	3.0	115	0.16	319
Central Europe						
2010-10-01	60° N	0° W	1.0	21	0.38	372
2010-10-02	64° N	11° W	1.0	46	0.75	778

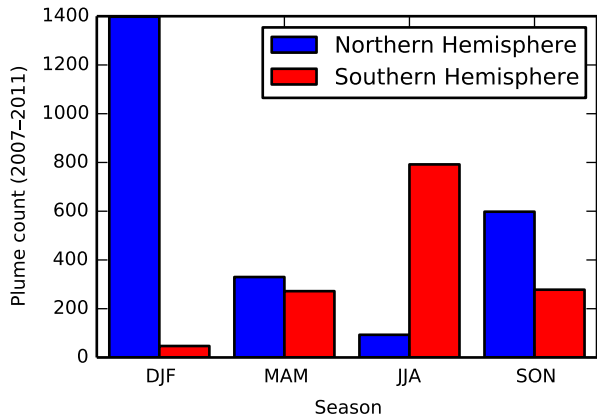


Fig. 15. Number of verified long-range transport plumes found by the detection algorithm in 2007–2011. There is a strong seasonality in both hemispheres, with a strong peak in local winter.

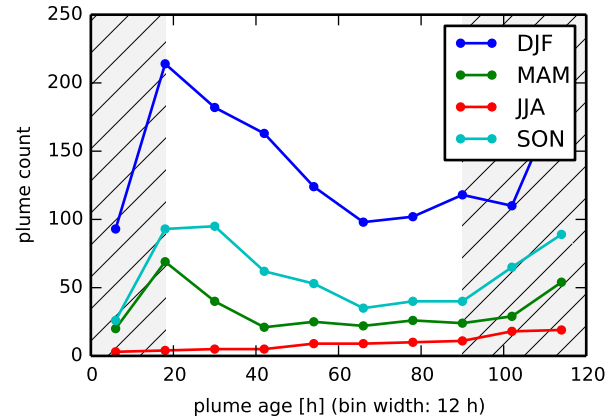


Fig. 17. Plume age at observation time of long-range transport events for 2007–2011, divided by season. The distribution illustrates the exponential decrease of long-range transport detections with age in the center. Two biases of the detection algorithm affect the hatched areas for low and high ages. See the text for details.

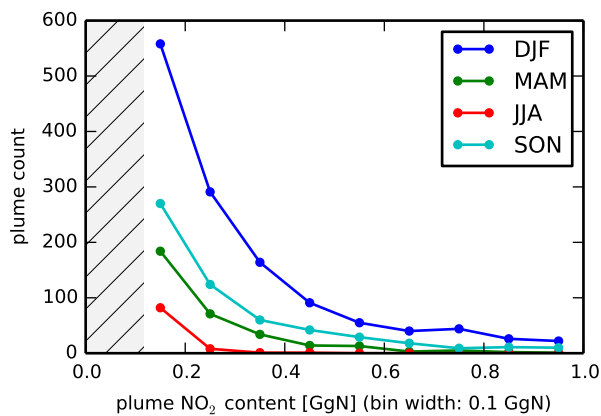


Fig. 16. NO₂ content of long-range transport events in the Northern Hemisphere, for different seasons. Note the lower mass limit of 5×10^{30} molecules (hatched area, corresponding to 0.12 Gg N).

winter follow a distribution that leads to much higher NO₂ content than in spring and (derived visually from Fig. 16) in summer. This supports cyclones and low temperatures as favorable conditions for long-range transport.

Further analysis reveals that this distribution is relatively stable across the five years investigated. We did not detect any significant trend in the mass distributions.

The observed NO₂ content distribution is a result of the NO₂ content distribution at the time of emission and the age distribution coupled with the lifetime of NO₂ in such events. Plumes observed on multiple days will appear multiple times in this statistic.

The estimated age of the plumes (Fig. 17) follows a distribution that appears to be the result from three independent effects:

- We find few plumes having ages of less than 24 hours, as not many plumes will have fully separated from their emission region in this short time period. They are thus still residing in the area of the emission region’s outflow, where high NO₂ vertical column density variability impedes their detection.
- After the age distribution reaches a maximum at about 18 hours, the plume ages appear to be dominated by a decaying function which most likely results from dissociation, wash-out and dispersion of NO₂. This makes a detection by the algorithm less probable and incorporates a boundary between a plume and background NO₂.
- After about 96 hours, the distribution increases again. This is probably a bias resulting from our detection algorithm. A higher plume age increases the chance of backtrajectories hitting an emission region. This may lead to an increase in false positive detections for high plume ages.

The distribution partly resembles a cumulative distribution function, as individual plumes may be observed on multiple, consecutive days (see Sect. 5). Plumes with an age approximately 24 h apart might actually be observations of the same plume on consecutive days. This effect is corrected for in the regional statistics (Sect. 6.3).

The altitude distribution (Fig. 18) behaves as expected: all plumes less than a day old reside at low altitudes, near

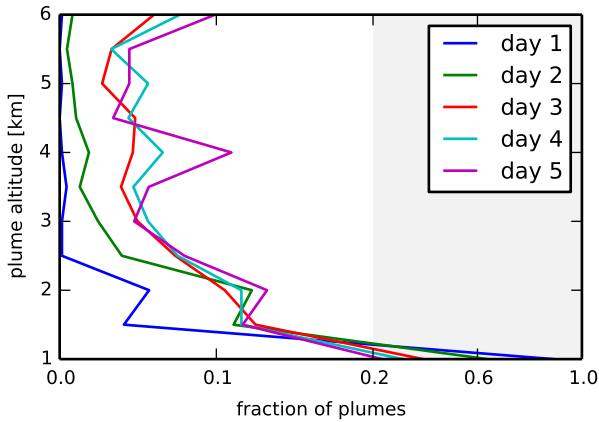


Fig. 18. Altitude distribution of NO₂ long-range transport plumes over the 11 altitude levels sampled in the HYSPLIT backtrajectories. Shown are the graphs for plumes younger than one day, between one and two days of age, etc. While most young plumes reside on the lowest level, they tend to distribute more equally in altitude over the following days. Note the compressed axis for fractions¹²⁵⁰ higher than 20%.

their emission region. The plumes shift to higher altitudes on¹²⁵⁵ the second day. After that, the distribution broadens as long-range transport events take different paths. The distribution suggests, that – to minimize systematic errors – we might improve our NO₂ vertical column densities by employing a lower altitude range for the calculation of reflectivities and¹²⁶⁰ air-mass factors – both in presence and absence of clouds. However, as we have shown the impact of this deviation is small.

Investigations into the distribution of the area encompassed by long-range transport plumes shows that plumes¹²⁶⁵ of an age of two to three days at observation time cover the largest area (not shown). This indicates that plumes start with high NO₂ concentrations and sharp boundaries, expand over a couple of days until the boundary of the plume gets blurred and the NO₂ content decreases.¹²⁷⁰

6.2 Routes and sources

When browsing through the GOME-2 NO₂ data manually,¹²²⁰ long-range transport events tend to appear in particular regions and follow particular paths. With the derived dataset, we now verify this in a quantitative manner.

The first obvious analyses are the determination of the typical routes and their quantitative strength. To achieve this, we select the detected plumes from every day of observation and¹²²⁵ project their respective NO₂ content onto a global map. We sum up the NO₂ content from all plumes. This gives the total vertical column density of NO₂ in long-range transport events on a global map. Then, we divide by the total number

of observations in the GOME-2 data set 2007–2011 for that particular grid cell (0.5° × 0.5°). This way, we obtain a global map of the 5-year mean vertical column density of NO₂ in long-range transport events.

This will include plumes measured on multiple days and lead to an appropriate representation of the routes of longer-lasting plumes.

We perform this analysis for four seasons to illustrate the local seasonality of the phenomenon. The results can be seen in Fig. 19.

The data confirm the existence of hotspots of NO₂ long-range transport events in the mid-latitudes and typical transport routes along which NO₂ plumes travel. Note, that our algorithm only detects events over the ocean and routes over continental areas cannot be detected. This rules out thunderstorms and other individual events of NO₂ emissions as the dominant origin of events identified as long-range transport in this study. They may still be present as false positives.

There is a strong seasonality in the data. Plumes are most dominant in local autumn and winter and can only rarely be seen in local summer. Due to observational limitations, especially the route of North American and European plumes towards the Arctic cannot be fully observed in the data. However, the data strongly suggest export of European and North American NO₂ to Greenland and onto the Arctic Ocean where it might alter tropospheric chemistry.

Long-range transport events are only observed in mid- to higher latitudes (starting roughly at ±40° N) where cyclones are frequent along the storm tracks and the lifetime of NO₂ is sufficiently long to allow transport over multiple days. We detect no significant long-range transport events in the tropics.

While China exports NO₂ quite frequently, not much of it is seen crossing a significant portion of the Pacific. Most of the plumes appear to be entering Russia after a brief journey over the ocean. This circular motion is typical for plumes in the Northern Hemisphere – North America and Europe show it to a lesser extent – and can be attributed to the cyclones transporting the plume.

We identify the sources of NO₂ long-range transport events by creating a similar map (Fig. 20). Here, we project the NO₂ load of each pixel onto its origin, as determined by the last point in its backtrajectory. This produces a rough map of the relative source strength for NO₂ emitted into plumes of long-range transport events by that particular region. ~~We show the map in –~~

We identify the following hot-spots: East Coast of North America, Central Europe, China, South Africa. Besides that, some plumes are also emitted from Argentina and Australia which only play a minor role. Europe is the only region which exhibits westward travel of plumes over the ocean.

~~The observations – It is not clear if all plumes in South Africa indicate that some of the plumes might also originate in – originate from the Highveld plateau or if individual~~

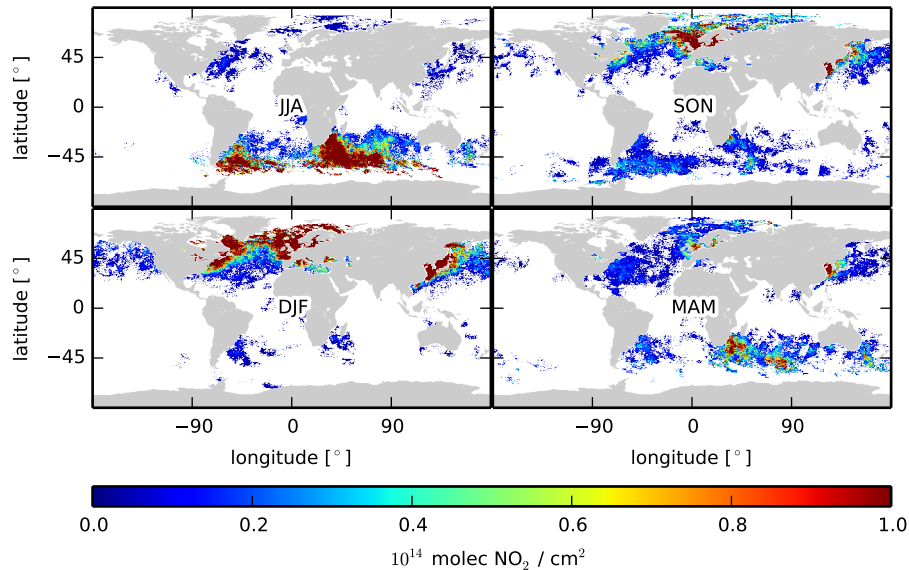


Fig. 19. Seasonal maps of the mean vertical column density of NO₂ observed in plumes associated to long-range transport events. Note that columns near Europe are always higher than columns near North America – at least partially due to its special geography.

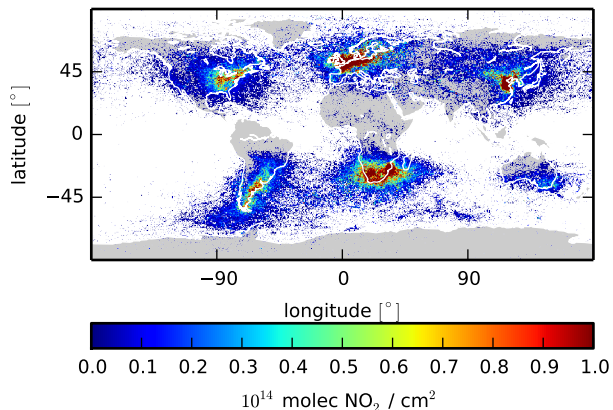


Fig. 20. Regional contribution to average NO₂ vertical column densities observed in long-range transport plumes. Sources of most long-range transport events are clearly visible. The high scatter originates from the low resolution of meteorological data used for the backtrajectories and uncertainties in the determination of the most likely backtrajectory.

likely due to the elevated emissions and descending wind following the geography from the plateau down to the ocean.

Even though we use only verified long-range transports, the emission data are highly scattered. This is due to the chaotic deviations resulting from long backtrajectories in strong wind shear. The coarse resolution necessary for this study amplifies this effect. Keeping this in mind, it is surprising, how sharply the emitters of long-range transports observed over the ocean are localized.

Investigations into the sources for plumes at different observed ages show that sources for plumes in their first day are sharply defined and the determined sources become more scattered with each day of plume age.

Fig. 21 shows an analogous map to Fig. 19, but here the NO₂ vertical column densities in long-range transport plumes are averaged over all seasons and instead binned by their respective plume age to show the temporal evolution of the routes. As expected, we find plumes with older ages at observation time at a larger distance from the emission regions and spread out more broadly than the young plumes. Also, the large number of plumes in the Baltic and North Sea, enclosed by emission regions (see Sect. 5.4), is apparent.

6.3 Regions

There are four major regions emitting NO₂ long-range transport events on the globe: the North American East Coast, Central Europe, South Africa and China. We have analyzed the plumes from these regions in further detail to gain more insight into the atmospheric conditions during long-range

observed plumes also originate from bush fires on the West Coast, while most stem from the Highveld plateau. These would only be a weak contribution to the overall signal which will be dominated by the strongly emitting Highveld industrial region and power plants. A large fraction of backtrajectories end on the coast East of the plateau. This is most

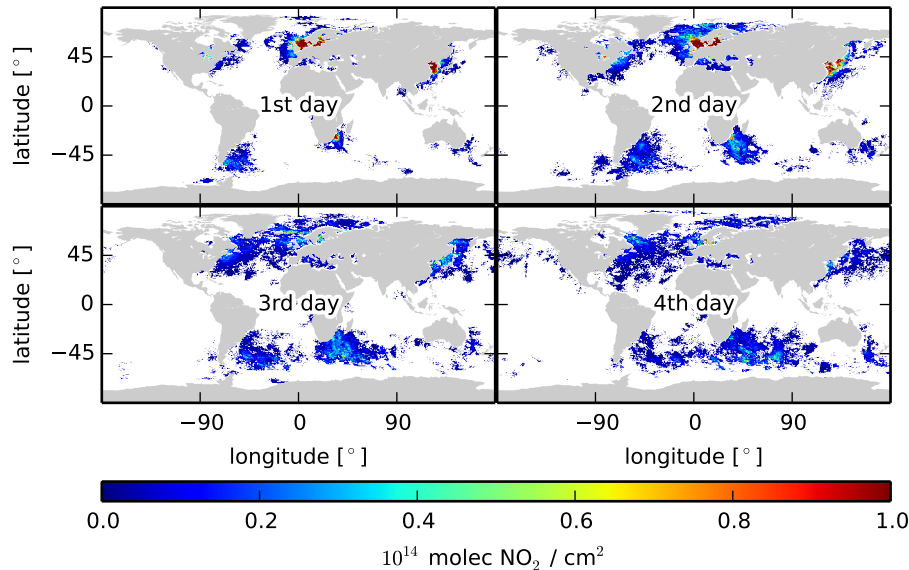


Fig. 21. Map of the mean NO₂ vertical column density observed in plumes of long-range transport events, binned by the age of plumes since emission at observation time.

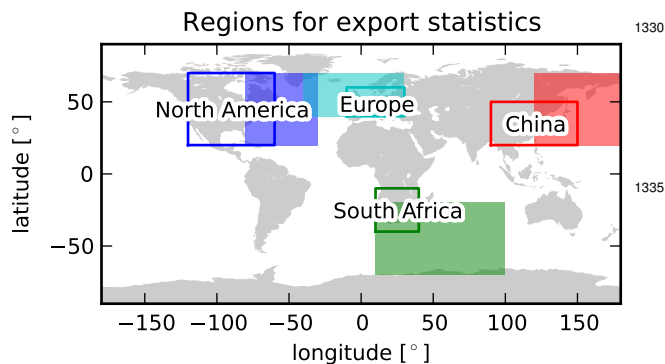


Fig. 22. The regions used for the statistical study. Only plumes are considered that were observed over the ocean in the filled rectangle and were found over land-masses in the open rectangle 24 hours earlier.

transport events and to quantify their impact on the global NO₂ distribution. The regions are highlighted in Fig. 22.

For each region, we only select plumes that moved from a continental area in the emission region out to the ocean in the observation region within the last 24 hours. This way we make sure that no plumes are counted twice and we only select plumes that actually originate in the selected hot-spot region.

The frequency of long-range transport events differs strongly from region to region. North America and Europe

emit a plume every 10 days on annual average, which corresponds to one plume every 5 days during winter. In contrast to that, South Africa emits plumes only every 17 days, while China emits one plume a week. This illustrates that NO₂ long-range transport is not a rare phenomenon and has been hidden from systematic scientific scrutiny only by cloud-filtering of satellite data.

6.3.1 Boundary NO₂ flux

First, we analyze the boundary flux of these regions. We sum up the NO₂ content of all the plumes in the respective region and normalize by the number of days of observation. This yields the total yearly export of NO₂ from the continent onto the ocean.

The data in Fig. 23 show, that the strongest emitter of plumes is China, followed by Europe. However, the plumes from China do not last as long and do not form such a prominent route. It appears that South Africa experiences the opposing effect: here, plumes follow a very stable and visible route over the open ocean. This leads to small absolute emissions being strongly represented in the dataset.

The total outflux of these four regions amounts to more than 50 GgN/a in long-range transport events, which are exported to the ocean and remote regions. This is slightly more than a permil of the estimated global yearly NO₂ emission rate of 43 TgN/a. This might appear to be a small fraction, but it constitutes a significant amount for such an unstable gas – especially, as our backtracing algorithm does not take

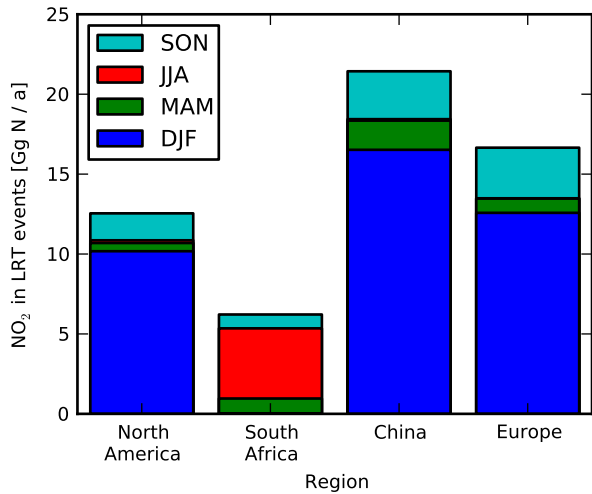


Fig. 23. Total yearly NO₂ content in long-range transport plumes emitted in the regions shown in Fig. 22 for different seasons.

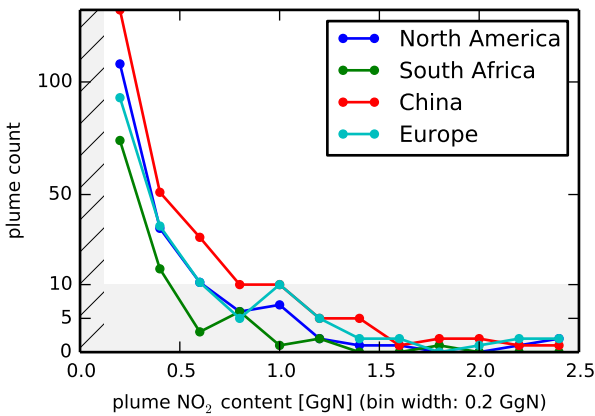


Fig. 24. NO₂ content distribution of long-range transport events observed in the respective regions. South Africa has the smallest plumes, while Europe emits a large fraction of NO₂-rich plumes. The data are binned in steps of 0.2 GgN. The hatched area denotes the NO₂ content below which plumes are not included in the analysis. The shaded area indicates a stretched axis to illustrate the frequency of plumes with high NO₂ content.

the decay of NO₂ from emission to observation of the plume into account.

We also look at the regional differences in plume sizes. Fig. 24 shows that China and especially Europe emit a relatively large fraction of NO₂-rich long-range transport plumes. North America and South Africa tend to produce much smaller plumes.

6.3.2 Composite analysis of meteorological conditions

Finally, we take a look into large-scale meteorological conditions which accompany long-range transport events, using NCEP DOE AMIP-II Reanalysis data. We use a composite analysis which has been used in similar studies to analyze polar lows in the nordic seas and NO_x transport in South Africa.

For each long-range transport event that we find in the given region, we collect meteorological conditions for various temporal offsets: two days before the plume has been emitted (according to backtrajectories) until the date of observation. For each offset we iterate over all retrieved long-range transport events and collect the meteorological conditions at the respective offset from emission (we call this the related composite). All remaining observations are collected in the unrelated composite. This allows an analysis of the temporal evolution of the conditions and yields insight into the dominant meteorological conditions behind long-range transport events.

We allow for multiple observations of the same plume to enter the dataset as these stronger and more reliable events are a better indication of favorable conditions.

We restrict the analysis to the respective winter seasons: December, January and February (DJF) in the Northern Hemisphere; June, July and August (JJA) in the Southern Hemisphere. These are the months with the highest long-range transport event frequency and thus most suited to investigate the associated meteorological conditions.

Now, for various meteorological quantities, we have two disjoint sets of observations (or composites): observations related and unrelated to plume emission. The unrelated composite represents the climatological mean in the absence of NO₂ long-range transport events. We calculate the deviation of the average of both the related and the unrelated composite. Also, we use the Mann-Whitney U test to find significant deviations in the two distributions.

We perform this test for the mean sea level pressure, the geopotential height at 500hPa, surface air temperature, both our custom cloud product and the FRESCO+ cloud fraction and the NO₂ vertical column density. Note that for the composite analysis, we did not interpolate values from NCEP DOE AMIP-II Reanalysis and GOME-2 and instead selected the nearest time step in the respective data set. This may lead to temporal discrepancies of up to 12 hours between the two data sets as we evaluate GOME-2 data only once a day.

North America (not shown) shows only very weak anomalies in these data — showing a slightly higher pressure over the central Atlantic — which do not provide further insight into the development. Note, that the results from this analysis only show anomalies in the mean of these quantities. Movement of the anomaly over time does not have to result from a movement or other type of temporal evolution of signals in the meteorological input data. They could be merely a coincidence or result from a superposition

of multiple patterns in the input data. However, a dominance of a single pattern in the input data will lead to this pattern appearing in the composite data.

One of the most prominent emitters, North America, does not show any regular pattern that would yield insights into the process that leads to the emission of long-range transport events. There are not even systematically elevated NO₂ vertical column densities which are typical of long-range transport events. Most likely, this lack of systematics is due to a relatively broad region of high NO₂ emissions. When meteorological data from plumes from varying origin are superimposed, this will lead to diminishing systematics, leading to little or no significant signal.

In South Africa, we find that in the days preceding leading up to and following the emission of the a long-range transport plume, there is a significant (likelihood > 99%) alternating pattern of sea-level pressure anomalies pattern of alternating high- and low-pressure anomalies moving towards the East (Fig. 25) in the region of 30–60°S surrounding the Antarctic continent. These anomalies are of the order $|\Delta P| \approx 2\text{--}5\text{ hPa}$ and move eastwards during the lifetime of long-range transport events, indicating a low-pressure anomaly approaches South Africa and crosses the southern tip of the African continent one day after plume emission. Over the course of plume emission, this anomaly increases in strength. This anomaly indicates that, typically, passing low-pressure systems passing South Africa – or cyclones – lead to the emission of an NO₂ plume. As on the Southern Hemisphere cyclones rotate clockwise, this indicates that NO₂ plumes would typically be ejected from South Africa on a south-eastwards trajectory. This is confirmed in the statistical analysis.

Composites of GOME-2 observations show elevated NO₂ vertical column densities over the Highveld plateau, moving to the South-East over the lifetime of a long-range transport event (Fig. 26). After the plume is emitted, NO₂ vertical column densities show an anomaly towards lower values in the Highveld region, which indicates that NO₂ has actually been relocated. Strong fluctuations in NO₂ vertical column density are visible near polar night, where only few observations enter the data and GOME-2 observations show higher uncertainties.

In Europe (Fig. 27), the situation is similar. In the days preceding a long-range transport event there is significantly a strong anomaly towards reduced mean sea-level pressure over Western Europe of the order $\Delta P \approx -4\text{--}-8\text{ hPa}$, $\Delta P \approx -5\text{ hPa}$. Contrasting this low-pressure anomaly, there is a high-pressure anomaly over the Arctic and Western Russia. These two anomalies form a channel which denotes the typical route observed in long-range transport events in this study. There is a significant low surface temperature anomaly over Europe and northern Russia in the preceding days, of order $\Delta T \approx -2\text{--}-5\text{ K}$. Additionally, in the composite, we observe regions of higher pressure over Scandinavia,

which extend up to the Arctic on subsequent days. These patterns are stationary and indicate high wind speeds towards the North-West in the transition region between the high- and low-pressure pattern. This represents the dominant route of European long-range transport plumes; we find in this study during the days of transport, of order $\Delta T \approx -1\text{--}-3\text{ K}$.

have shown in simulations that the North Atlantic Oscillation (NAO) may be responsible for transport of pollutants to the Arctic, modeling trace gases with lifetimes of 5 days. find similar patterns of pollution export as shown in Fig. 19 to stem from zonal wind flow, resulting from the NAO. However, the results in Fig. 27 indicate a possible negative correlation to the NAO, with emissions of plumes being linked to a negative NAO index – showing a high-pressure anomaly over Iceland and a low-pressure anomaly over the Azores. The high-pressure anomaly over Iceland is, however, spatially extended, making these results ambiguous.

A correlation of plume frequency with monthly NAO indices from the NCEP Climate Prediction Center (<http://www.cpc.ncep.noaa.gov/products/precip/CWlink/>) over all months (Fig. 28) shows no significant correlation and shows no NAO characteristics (probability of a random distribution generating such data: 32%). However, these two quantities exhibit two features: an uncorrelated part when few plumes are emitted and a highly correlated part when multiple plumes are emitted. When we remove all points with less than 5 plumes in the given month, the probability of a random distribution leading to these results is only 0.05%, making this result highly significant. Plume emission rates significantly increase with a lower NAO index. This confirms results from the composite analysis. Negative NAO indices with low plume frequency are almost entirely spring to late summer, which are unfavorable for NO₂ long-range transport due to radiation budget.

For long-range transport events originating from Europe, again, we find significantly elevated NO₂ vertical column densities over Europe, the North Sea and the North East Atlantic during the course of emission (Fig. 29).

Lastly, in China we find that the sea-level pressure a strong upwards anomaly of NO₂ vertical column densities in the Beijing area in the days preceding an event shows features of atmospheric oscillation. There is a significant high-pressure anomaly over Greenland which moves over to the Russian Arctic Ocean during the long-range transport event, as well as a low over East Russia and highs and lows near Antarctica.

Again, China does not show any significant increase in the emission of a long-range transport event. This anomaly only partly moves and dissolves after the emission. Long-range transport events are more likely to be observed when there are elevated NO₂ levels. However, China is the only region where we find a significant anomaly in the FRESCO+ cloud fraction. In the days preceding and

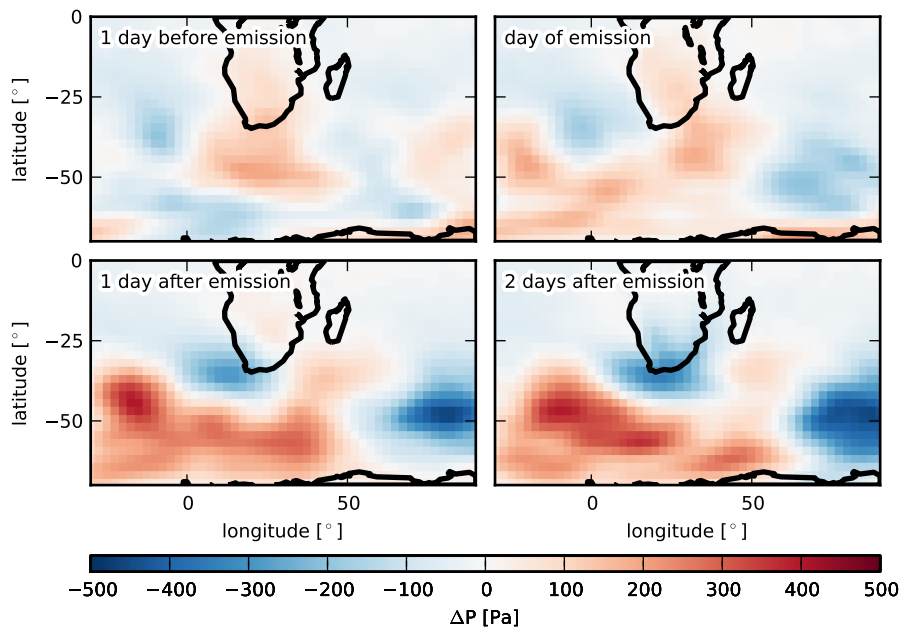


Fig. 25. NCEP DOE AMIP-II Reanalysis mean sea-level pressure anomaly (given in Pa) for the days of plume emission in the South African region. Only events in JJA (2007–2011) are shown, to prevent biases from meteorologic seasonality. ~~99-significance contours from the Mann-Whitney U-test are depicted in magenta.~~ The image shows significant high and low pressure patterns in the southern midlatitudes, moving from West to East.

during the event, there is a region of significantly enhanced cloud coverage moving from the Beijing area out to in the source regions. There is also a low-pressure anomaly over the Okhotsk Sea and the ocean. The increase in cloud fraction is quite substantial: it increased by about 0.3. This would rule out all the corresponding pixels in a regular cloud-filtered Kamchatka peninsula which is shifted to northern China over the course of the transport. This anomaly does not stay as concentrated after the emission and spreads over East Asia (Fig. 30).

These findings suggest that passing low-pressure systems or cyclones may be the dominant process leading to NO₂ long-range transport events in mid-latitudes. Elevated NO₂ data set. This, again, indicates that long-range transport events from China are also associated to frontal systems concentrations in source regions are linked to the detection of these events.

7 Conclusions

We analyzed NO₂ long-range transport events globally using GOME-2 satellite data. For this, we had to take observations with cloudy scenes into account. We employed a simple approximation to determine the NO₂ vertical column density under cloudy conditions for an elevated plume.

We developed an algorithm that automatically identifies long-range transport events in these data. It detects short-lived positive anomalies of NO₂ vertical column densities over the ocean and performs lagrangian backtracking to verify the anthropogenic origin of the event and to assess further plume properties. We then analyzed the resulting dataset of 3808 long-range transport events in GOME-2 data from 2007 to 2011.

We cannot distinguish NO₂ from anthropogenic sources and LiNO_x. However, their high frequency, distinguished seasonal and geographic distribution and the visibility of the observed events indicate that the majority of events found in the satellite data is not caused by thunderstorms, as LiNO_x is rarely visible in observations of DOAS satellite instruments.

We found that NO₂ long-range transport events are a common phenomenon. There are four major hot-spots which emit NO₂ plumes subject to long-range transport: the North American East Coast, South Africa, China and Europe.

The NO₂ plumes travel along characteristic routes, leading to the polar circle for South Africa and into the Arctic for North America and Europe. The total amount of NO₂ transported in these events is surprisingly large considering the short lifetime in the boundary layer, where most emissions take place. Reservoir species of NO₂ are not detected and their likely presence will lead to an underestimation of the potential NO₂ impact on downwind regions. The actual

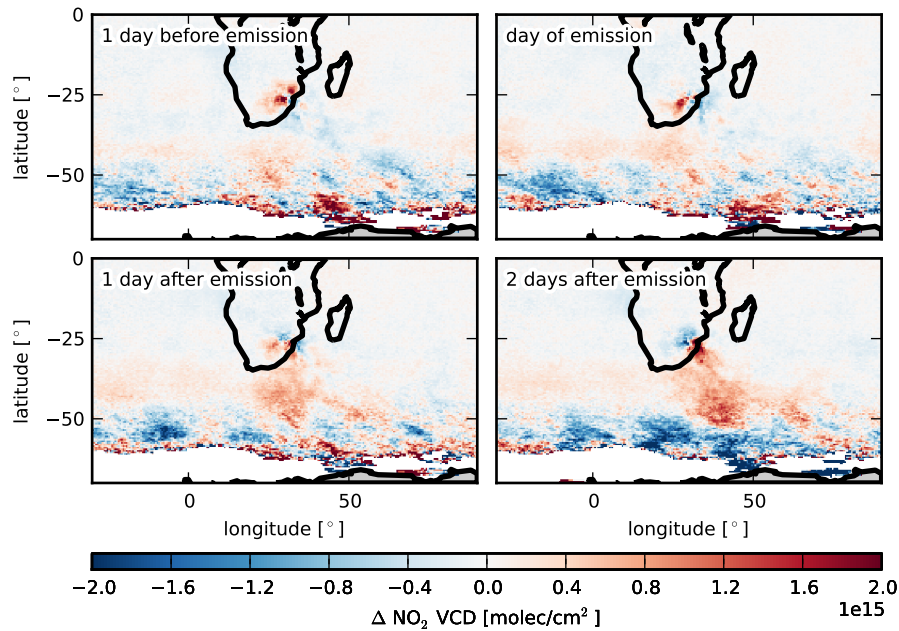


Fig. 26. As in Fig. 25, but showing anomalies in GOME-2 tropospheric NO₂ vertical column densities for the days of plume emission in the South African region. Only events in JJA (2007–2011) are shown, to prevent biases from meteorologic seasonality. There is an anomaly towards high values over the Highveld region before plume emission, moving to the South-East during the long-range transport event. After emission, the NO₂ vertical column densities over the Highveld region are on average lower, while an upwards anomaly can be seen southeast of South Africa. High fluctuations in the GOME-2 data and few observations result in visible noise in the anomalies near polar night.

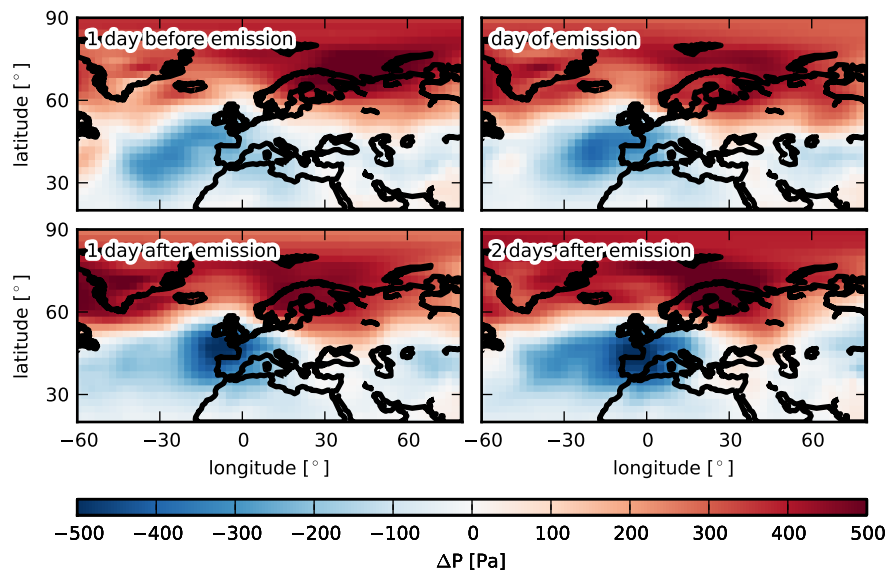


Fig. 27. As in Fig. 25, but for the Central European region. Only events in DJF (2007–2011) are shown. The image shows significant stationary high and low pressure patterns in data show a low-pressure anomaly over Western Europe over the course of the transport. Contrasting this, there is a high-pressure anomaly over the Arctic and over Europe/Northern Russia.

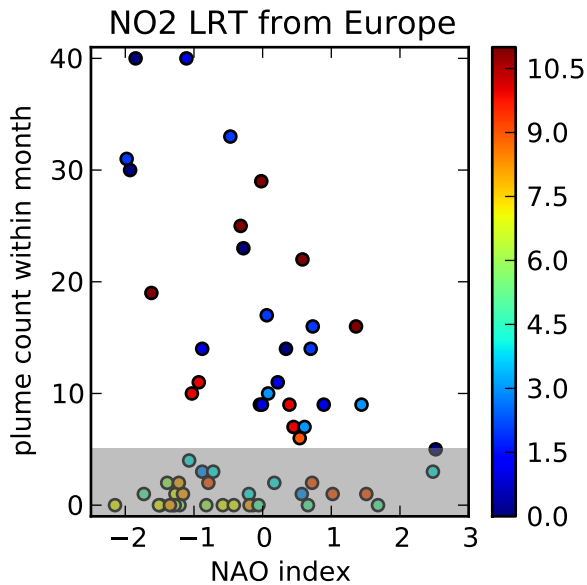


Fig. 28. Correlation of plume frequency in a given month with the NAO index as determined by the NCEP Climate Prediction Center. Colors denote the calendaric month (with 0 being December). Values in the shaded area were not considered for the correlation analysis. There are two superimposed features: no correlation during spring to late summer and a strong negative correlation during autumn and winter.

impact on atmospheric chemistry of downwind regions will depend on the abundance of O₃, OH and NO₂, among others. Unfortunately, GOME-2 satellite data do not permit an analysis of these processes-transport events and their impact in the Arctic, which is likely to be one of the most sensitive regions to the effects of altered atmospheric and oceanic chemistry due to NO₂ long-range transports.

The emission shows strong seasonality, both in number and size of the plumes. More and larger plumes are emitted in winter, when the lifetime of NO₂ is long, anthropogenic emission rates are especially high and meteorological conditions are favorable with frequent cold fronts and cyclones. No long-range transport events have been identified in the tropics.

The meteorology responsible for these events appears to depend on the region. In North America, plumes follow storm tracks over the Atlantic, but show no distinct meteorological anomaly in a composite analysis. In Europe, Arctic highs and European lows appear to favor long-range transports towards the Arctic. South Africa shows a typical pattern of alternating high and low pressure systems moving eastwards linked to plume emission.

It is likely that many events are triggered by a cyclone passing the emission region, accompanied by a cold front which lifts the NO₂ upwards into the free troposphere. There,

wind speeds tend to be higher and the lifetime of NO₂ increases to the order of days, which is consistent with what we find in observations, simple estimates from our analysis. Plumes can keep their distinct boundaries over days before they dilute.

Besides events from anthropogenic sources, we also observe events from Australia which appear to be caused by bushfires in the south of the continent. In at least one case, there is evidence that lightning occurred during a long-range transport event and might have added NO₂ to the plume, most likely leading to an overestimation of the lifetime and transport of anthropogenic NO₂.

NO₂ long-range transport events can transport air pollution from South Africa to Australia, from China to Japan and Taiwan and they are likely to have an impact on remote, pristine regions such as the Arctic.

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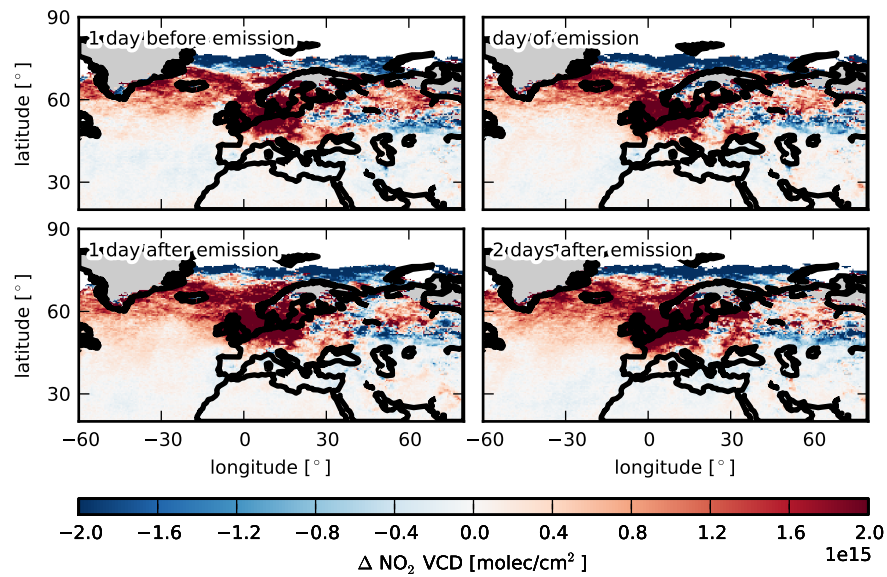


Fig. 29. As in Fig. 26, but for Europe and the North Sea. Only events in DJF (2007–2011) are shown. The data show significantly elevated levels of NO₂ vertical column density over Europe and the North Sea in the days before and during a long-range transport event.

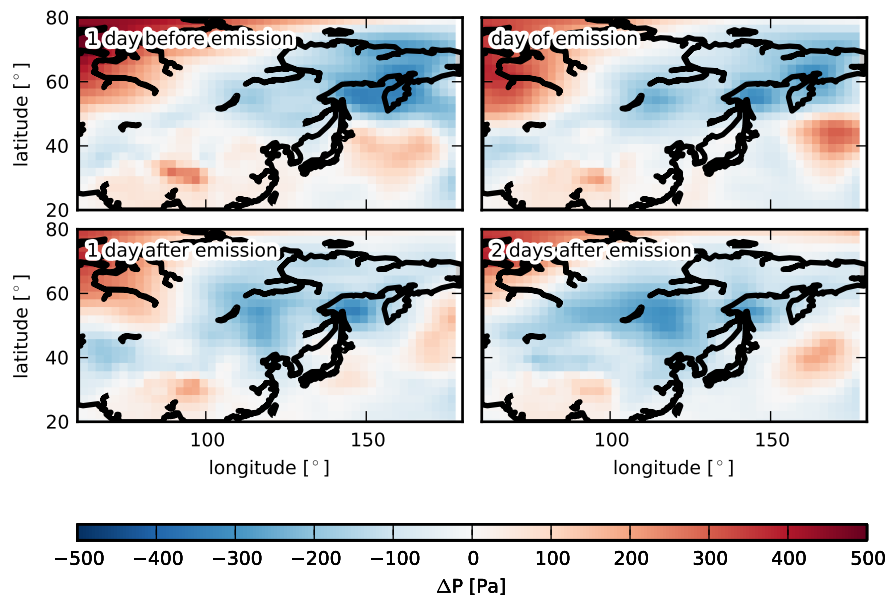


Fig. 30. As in Fig. 25, but for China and the Pacific. Only events in DJF (2007–2011) are shown. The data show a low-pressure anomaly moving from Russia towards northern China during the days preceding and following plume emission.