Re.: Revised manuscript “Unexpected long-range transport of glyoxal and formaldehyde observed from the Copernicus Sentinel-5 Precursor satellite during the 2018 Canadian wildfires”.

Dear Dr. McLaren,

we would like to take the opportunity to thank you again for accepting the editorship of our manuscript “Unexpected long-range transport of glyoxal and formaldehyde observed from the Copernicus Sentinel-5 Precursor satellite during the 2018 Canadian wildfires”.

We noticed a small mistake in the discussion manuscript. For the AMF calculation in the CHO.CHO and HCHO satellite retrievals, we accidentally used wrong units in the profiles used for the simulations, which created some background offset between different days. In the revised manuscript, we corrected the CHO.CHO and HCHO VCDs. This introduces only relatively small changes in the magnitude of CHO.CHO and HCHO compared to the dataset shown in the discussion manuscript and thus not affect the interpretation of the results.

Please find attached a revised version of our manuscript, the answers to the referees, as well as the manuscript with color-coded changes showing the differences to the original version. We have answered point by point the comments and suggestions of each referee.

We hope that with the submission of the author comments and the revision of the manuscript, our article will be accepted for publication in ACP.

If possible, we would also like to ask to include this manuscript in the TROPOMI special issue (https://www.atmos-chem-phys.net/special_issue400_1002.html)

Yours sincerely,

Leonardo Alvarado (on behalf of the co-authors)

List of attachments:
- Author comments to Referee #1
- Author comments to Referee #2
- Revised manuscript with highlighted changes (color-coded)
- Revised manuscript
Author reply to comments of anonymous Referee #1 on the manuscript
“Unexpected long-range transport of glyoxal and formaldehyde observed from the
Copernicus Sentinel-5 Precursor satellite during the 2018 Canadian wildfires”

Leonardo M. A. Alvarado et al.
December 13, 2019

We would like to thank the anonymous referee #1 for carefully reading our manuscript and
providing valuable comments, which helped to improve the quality of our manuscript. We have
answered below point by point to each comment.

We noticed a small mistake in the discussion manuscript. For the AMF calculation in the
CHO,CHO and HCHO satellite retrievals, we accidentally used wrong units in the profiles used for
the simulations, which created some background offset between different days. In the revised
manuscript, we corrected the CHO,CHO and HCHO VCDs. This introduces only relatively small
changes in the magnitude of CHO,CHO and HCHO compared to the dataset shown in the
discussion manuscript and thus does not affect the interpretation of the results.

Legend:
- referee comments
- authors comments

This paper presents satellite-derived observations of glyoxal and formaldehyde from the TROPOMI
instrument, over British Columbia, Canada. Elevated column densities were associated with fire
hot-spots and observed over distances of up to 1500 km. Based on comparisons with FLEXPART
simulations with different lifetimes, effective lifetimes of >20 hours are required to explain the
observations. The authors indicate that the effective lifetimes are in contrast to the shorter
expected lifetimes of these species.

My main concern with the paper is with the references to the lifetimes of glyoxal and formaldehyde.
The paper does not provide adequate evidence to support the determination of atmospheric
lifetimes, mainly because chemistry and deposition are not considered (and as the authors state,
not within the scope of this paper). The observations of glyoxal and formaldehyde enhancements
downwind of the fire hot spots are likely due to formation (and loss) processes (as the authors also
note) and thus, reference to lifetimes accounting only for transport time is not appropriate.

We agree that full chemical simulations along the trajectory would enhance our understanding of
the chemical transformation taking place as the fire emissions are transported. However, we
consider the focus of this study was slightly different. We present simultaneous observations of
CHO,CHO, HCHO, NO$_2$ and CO in plumes coming from wildfires. The FLEXPART simulations
describe how the air masses are physically transported from the source of production, in this case,
the fires. They are coupled with estimates of the lifetime of a theoretical tracer species travelling in
the transported air mass. Our initial assumption, that the formaldehyde and glyoxal were produced
in the fire and then transported and chemically removed, primarily by photolysis and reaction with hydroxyl radicals, clearly does not explain the observed formaldehyde and glyoxal temporal evolution. We consider that FLEXPART simulations provide an important piece of information to help us understand the behaviour of air mass plumes, as they are transported. To avoid confusion we have clarified in the text the objectives of the modelling and our use of the term “effective lifetime” in this study.

This is a relevant paper for ACP and would be of interest to ACP readers. The paper is comprehensive, well written with clear study objectives, logically presented and articulated conclusions. The satellite-derived observations of glyoxal and formaldehyde far downwind of the fire sources are quite interesting and can stand on their own without comparison to ‘expected’ lifetimes.

I recommend acceptance to ACP after addressing the above comments and a few minor comments below.

Thank you very much for your positive comments.

L42: biomass burning includes wildfires – what is meant by indicating both?

The sentence has been removed. What we intended to express here is that pyrogenic emissions include wildfires and agricultural fires.

L49: transported to ‘those’ regions – please clarify or reword

Done

Intro – break into paragraphs for easier reading

Done

L117 – any comment on the uncertainty associated with using an aerosol profile to depict the glyoxal profile?

Quantification of uncertainty associated with the assumed profile is difficult at it depends on several factors such as the geometry of observation, the presence of clouds, the altitude of aerosols, the surface albedo, etc. For this study, we consider that the most accurate approach is assuming a vertical distribution of glyoxal similar to the one measured for the aerosols. This is because no significant contribution from other sources is expected. If there is any contribution from layers close to the ground, it is shielded by the aerosol layers and difficult to detect by satellite under the conditions of the measurements in our case study. This is because the measurement sensitivity decreases below the aerosol layer as most photons are scattered back to the satellite before they can reach these altitudes (Leitao et al., 2010). Here, a sensitivity study has been conducted assuming glyoxal profiles at different altitudes and evaluating the impact on the glyoxal AMFs. Figure 1A shows glyoxal profiles with maximum concentrations at different altitudes. Figure 1B shows the AMFs dependence with SZA for different profiles. All AMFs behave quite similar, however, for layers at higher altitude the AMFs are larger than those for a layer closer to the ground. Relative differences between AMFs were also computed using as reference the profile with maximum concentration at 2 km. The AMFs vary between 15% and 30% for small SZA but larger deviations are found for large SZA, especially for profiles with a maximum at high altitude. In
general, uncertainty associated with the assumed vertical profile is one of the most significant sources of error in DOAS retrievals and can lead to uncertainties between 10 and 30% (Boersma et al., 2004; Lerot et al., 2010).

![A) Glyoxal profiles at different altitudes](image)

![B) Dependence of AMFs with the profile](image)

![C) Relative difference of AMFs for profiles at different altitude against the AMF for the reference profile](image)

Figure 1: A) Glyoxal profiles peaking at different altitudes. B) Glyoxal AMFs computed using the profiles of A). C) Relative difference of AMFs for profiles at different altitude against the AMF for the reference profile.

L122 – what is meant by a homogeneous distribution? The same profile is used over the geographic region studied?

Yes is the short answer. We assume that the aerosols are distributed homogeneously in the whole region. For each day, the mean aerosol profile is computed as the average of all aerosol profiles measured in the region after removing cloud-contaminated pixels, and this profile is then used in the retrieval of the trace gas data.

L131 – how much reduction in noise? Can this be quantified?

The random noise in the large fitting range is about 4 times smaller than the corresponding value obtained using a smaller fit window. In the figure below, a comparison of the variation of formaldehyde slant column densities over the equatorial Pacific is shown. In this area, HCHO is mainly produced by methane oxidation and therefore assumed to be homogeneously distributed. Variations in the retrieved HCHO columns are thus taken as indication of retrieval uncertainty. The scatter obtained using a large fitting window corresponds to about $4.5 \times 10^{15}$ molec.cm$^{-2}$, while the fitting window used by Vrekoussis et al., (2010) leads to a variability of about $1.6 \times 10^{16}$ molec.cm$^{-2}$. 
Figure 2: Distribution of S5P HCHO differential slant column densities over a clean equatorial area ocean region (5° S – 5° N, 150° – 210°) for August 2018.

L132 – ‘strong absorption of the latter’; of the latter not appropriate in this sentence, confusing. Remove ‘of the latter’ and clarify.
The manuscript has been modified accordingly.

L150 – confusing sentence regarding lifetimes....
The text has been modified in order to be clearer.

L156 – ‘exact emissions’; what is meant by this? emission type (pollutant?) or emission rate?
Here, we meant “emission rate”, which has been clarified in the revised manuscript.

L161 – reference should be in brackets
Done

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Leitão, J., Richter, A., Vrekoussis, M., Kokhanovsky, A., Zhang, Q. J., Beekmann, M., and Burrows, J. P.: On the improvement of NO2 satellite retrievals – aerosol impact on the airmass factors, Atmos. Meas. Tech., 3, 475–493, doi:10.5194/amt-3-475-2010, 2010.

Boersma, K. F., Eskes, H. J., and Brinksma, E. J.: Error analysis for tropospheric NO2 retrieval from space, J. Geophys. Res., 109, D04311, doi:10.1029/2003JD003962, 2004.

Lerot, C., Stavrakou, T., De Smedt, I., Müller, J.-F., and Van Roozendael, M.: Glyoxal vertical columns from GOME-2 backscattered light measurements and comparisons with a global model, Atmos. Chem. Phys., 10, 12 059–12 072, doi:10.5194/acp-10-12059-2010, 2010.

Vrekoussis, M., Wittrock, F., Richter, A., and Burrows, J. P.: GOME-2 observations of oxygenated VOCs: what can we learn from the ratio glyoxal to formaldehyde on a global scale?, Atmos. Chem. Phys., 10, 10 145–10 160, doi:10.5194/acp-10-10145-2010, 2010.
We would like to thank the anonymous referee #2 for carefully reading our manuscript and for providing valuable comments, which helped to improve the quality of our manuscript. We have answered below point by point to each comment.

We noticed a small mistake in the discussion manuscript. For the AMF calculation in the CHO,CHO and HCHO satellite retrievals, we accidentally used wrong units in the profiles used for the simulations, which created some background offset between different days. In the revised manuscript, we corrected the CHO,CHO and HCHO VCDs. This introduces only relatively small changes in the magnitude of CHO,CHO and HCHO compared to the dataset shown in the discussion manuscript and thus not affect the interpretation of the results.

This paper describes TROPOMI satellite retrievals of glyoxal (CHO,CHO) and formaldehyde (HCHO) over Western Canada during the wildfire-intensive month of August 2018. Enhanced VCDs of ~14x10^{14} molec cm^{-2} CHO,CHO and ~50x10^{15} molec cm^{-2} HCHO are observed at wildfire locations and these enhancements appear to persist over long distances of up to 1500 km. FLEXPART tracer transport simulations using GFAS emission locations are able to reproduce the spatial distribution of enhancements if a lifetime of 20 hours or more is used.

My general suggestion for the paper is to articulate more clearly the usage of lifetimes in FLEXPART to avoid confusion. Since a full chemical transport model is not being used, (1) the model is not producing CHO,CHO and HCHO columns that can be directly compared to the observations and (2) the ‘effective lifetime’ does not represent the chemical/physical production/loss processes that are occurring within the large wildfire plume. Rather, the ‘effective lifetime’ in FLEXPART simply allows tracer particles to persist from their origin and continue to be transported. This provides a general spatial comparison to the observations. Hence the ‘effective lifetime’ here is a simple and useful computational proxy – but not a representation of – complex plume processes. The authors have clarified this in the Methods but it should be made more obvious to readers in other sections.

For example, the wording in the abstract suggests >24 hour lifetimes during night-time or at high latitudes (does this refer to Canadian latitudes?) and presents 20+ hours as the FLEXPART lifetime; these are referring to the different usages described above and can be confusing.
The authors discuss the far downwind CHO, CHO and HCHO observations and suggest continued production from precursors as the likely cause, and not a physical increase in the lifetimes. It is worth noting that British Columbia is a coastal province and the presence of chlorine-initiated oxidation adds to the skepticism of >20 hr lifetimes.

We thank the reviewer for the comment. We agree that this study does not try to determine the current chemical lifetimes of these species, and the simulations are only used to describe how they are physically transported from the source of production. The estimated lifetime over which these species are observed in the atmosphere corresponds to the assumption of a simple exponential first-order decay which is not representative for the complex chemistry in the plume. We have clarified in the text what we mean by this effective lifetime in our study to avoid confusion. However, we believe that FLEXPART simulations provide an important piece of information for understanding the behaviour of the plume until it is dispersed.

Regarding the latitudes in the manuscript, these refer to Canadian latitudes. The lifetimes of VOC depend on the season and these are connected to OH variability, and thus to photolysis as well. Globally, OH significantly decreases for latitudes larger than 45°N (Leiheveld et al., 2016), which corresponds to Canadian latitudes, and thus we expect longer lifetimes for VOCs over these latitudes.

This is a relevant paper for ACP. The paper is well written and the results are presented in an organized manner. The satellite retrievals of CHO, CHO and HCHO from the recently launched TROPOMI instrument are highly valuable and provide improved insight into Canadian wildfires as presented in this work. I recommend acceptance to ACP after addressing the above comments and the minor corrections below:

Thank you very much for your positive comments.

Line 05 – ‘lifetimes’
Done

Line 24 – order of CHO and HCHO is awkwardly changed in this sentence
It has been rearranged in the revised manuscript.

Line 51 – remove comma after ‘Spectroscopy’
Done

Line 57 – remove comma after ‘07’
Done

Line 73 – ‘and/or’
Done

Line 81 – capitalize ‘Precursor’ and remove ‘of’
Done
Line 85 – remove ‘of’
Done

Line 86 – keep formatting of dates consistent (e.g. 13 October 2017 vs. August 07 2018 in Line 57 vs. 10th of August 2018 in Line 140, etc.)
The text has been modified in order to be consistent.

Line 89 – 13:30 LT
The manuscript has been modified accordingly.

Line 92 – again consider removing ‘of’
Done

Line 94/95 – keep formatting of in-text citations consistent
The manuscript has been modified accordingly.

Line 106 – How many CHO.CHO peaks are within this range?
In the fitting range used in this study, five glyoxal absorption peaks can be found (see Figure 2A in the manuscript), including the strongest absorption band of glyoxal.

Line 110 – What is meant by a ‘row-dependant’ spectrum? Explain. Is it one background spectrum per line of latitude? The author states that a daily mean is used but if the background spectrum changes throughout the day, will this introduce significant error?
Here, a daily background spectrum is computed by averaging over the whole latitude range (50° S – 50° N) for each across-track viewing direction individually. Thus, one background spectrum is used per viewing direction (450 spectra). This approach is taken to minimise small across-track dependent differences of the TROPOMI measurements.
Ideally, a solar irradiance measurement would be used as a background spectrum in the analysis. However, for weak absorbers such as glyoxal and formaldehyde, use of a daily Earth shine background derived by averaging measurements over the Pacific has proven to reduce noise and offsets in the data. Day to day changes of this background spectrum are small and are therefore expected to introduce only small uncertainties. However, over longer time periods (weeks and months), instrumental drift may induce changes in trace gas columns if the background spectrum is not based on recent measurements. Use of a daily background spectrum resulted in a significant reduction of instrumental noise similar to that demonstrated in previous studies (Schönhardt et al. 2008, De Smedt et al., 2008, Anand et al., 2015, Alvarado, 2016).

Line 110 – ‘...as a background spectrum (Alvarado, 2016).’
Done

Table 1 – remove ‘de’ in title
Done

Line 127 – heading should state ‘HCHO retrieval from TROPOMI measurements’ to match Line 93
Done
Line 133 – ‘consists’
Done

Line 161 – full citation in brackets
Done

Line 206 – remove comma
Done

Line 211 – ‘HCHO’
Done

Line 220 – reword to ‘...which are discussed in detail in Section 3.2.’
The manuscript has been reworded accordingly.

Line 229 – reword to ‘Figure 7 presents...’
The manuscript has been reworded accordingly.

Line 231 – ‘However, on the 20th...’
Done

Line 233 – ‘from’
Done

Line 252 – ‘references’
Done

Figure 8 caption – ‘...for the 10th of August 2018.’
Done

Line 286 – misspelling of ‘conclusions’ in heading
This has been corrected in the manuscript.

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Anand, J. S., Monks, P. S., and Leigh, R. J.: An improved retrieval of tropospheric NO2 from space over polluted regions using an Earth radiance reference, Atmos. Meas. Tech., 8, 1519–1535, 2015.

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Schönhart, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H. K., and Burrows, J. P.: Observations of iodine monoxide columns from satellite, Atmos. Chem. Phys., 8, 637–653, 2008.
Unexpected long-range transport of glyoxal and formaldehyde observed from the Copernicus Sentinel-5 Precursor satellite during the 2018 Canadian wildfires

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Abstract. Glyoxal (CHO.CHO) and formaldehyde (HCHO) are intermediate products in the tropospheric oxidation of the majority of volatile organic compounds (VOC). CHO.CHO is also a precursor of secondary organic aerosol (SOA) formation in the atmosphere. These VOCs CHO.CHO and HCHO are released from biogenic, anthropogenic, and pyrogenic sources. CHO.CHO and HCHO tropospheric lifetimes are typically considered to be short during the daytime and at mid-latitudes (few, e.g., several hours), as they are rapidly removed from the atmosphere by their photolysis, oxidation by OH, and uptake on particles or deposition. During nighttime, at high latitudes, lifetime can be prolonged, tropospheric lifetimes increase to many hours or even days. Previous studies demonstrated that CHO.CHO and HCHO can be vertical column densities, VCDs, are well retrieved from space-borne observations using the DOAS method, differential optical absorption spectroscopy, DOAS. In this study, we present CHO.CHO and HCHO columns VCDs retrieved from measurements of the TROPOMI instrument, launched recently on the Sentinel-5 Precursor (S5P) platform in October 2017. Strongly, we observed strongly elevated amounts of CHO.CHO and HCHO are observed during the 2018 fire season in British Columbia, Canada, where a large number of fires occurred in August 2018. CHO.CHO and HCHO plumes from individual fire hot-spots are observed in air masses travelling over distances of up to 1500 km, i.e. much longer than expected for the relatively short atmospheric tropospheric lifetime of expected for CHO.CHO and HCHO. However, the temporal evolution of the plume differs for both species. Comparison with Lagrangian-based FLEXPART simulations for particles with different lifetimes shows by the particle dispersion model FLEXPART indicates that effective lifetimes of 20 hours and more are needed to explain the observations, indicating that of CHO.CHO and HCHO if they decay in an effective first order process. FLEXPART used in the study calculates accurately the transport. In addition, an constant exponential decay, in our case assumed to be photochemical, of a species along the trajectory is added. We have used this simple approach to test our assumption that the CHO.CHO and HCHO are created in the fires and then decay at a
constant rate in the plume, as it is transported. This is clearly not the case and we infer that CHOCHO and HCHO are either efficiently recycled during transport, or continuously formed from the oxidation of longer-lived precursors present in the plume, or possibly a mixture of both. We consider the best explanation of the observed CHO.CHO and HCHO VCD in the plumes of the fire is that they are either efficiently recycled during transport or, continuously formed from the produced by oxidation of -longer-lived precursors, also released by the fire and present in the plume.

1 Introduction

Formaldehyde (HCHO) is produced in the oxidation of both methane (CH₄) and other Volatile Organic Compounds (VOC). Glyoxal (CHO.CHO) is the smallest alpha-dicarbonyl formed in the oxidation of most many VOC containing two or more carbon atoms. Although both HCHO and CHO.CHO and HCHO, which are known as OVOC (Oxygenated Volatile Organic Compounds) have similar rates of reaction with the hydroxyl radical (OH) in the troposphere, the photolysis frequency of HCHO, which absorbs and is photolysed in the ultraviolet-A (UV-A), is significantly smaller than that of CHO.CHO, which absorbs in the blue. As a result, the atmospheric lifetime of HCHO is longer than that of CHO.CHO (Atkinson, 2000). Both species are short-lived during daytime due to their rapid removal by photolysis and reaction with OH radicals (Atkinson, 2000; Volkamer et al., 2007). These processes are the major sinks of CHO.CHO and HCHO₂ contributing about 69% and 96%, respectively. The remaining part of HCHO being is removed by deposition (4%), while for CHO.CHO₂ 22% are removed by SOA formation and 8% by deposition (Stavrkou et al., 2009a, c). Additionally, HCHO and probably also CHO.CHO during nighttime can also be removed by reaction with nitrate (NO₃) radicals (Atkinson, 2000). HCHO and CHO.CHO and HCHO play a key role in tropospheric chemistry because they act as temporary reservoirs of VOC; additionally, they produce releasing carbon monoxide (CO) and HOx (OH and Hydroperoxyl, HO₂) free radicals, which participate in catalytic cycles creating and destroying tropospheric ozone (O₃).

The slant and vertical column amounts densities of HCHO were first observed from space using measurements from the GOME instrument (e.g. Burrows et al., 1999, and references therein). These columns were later used to estimate the emission strength of precursor VOC (Palmer et al., 2003; Abbot et al., 2003). The simultaneous observation of CHO.CHO and HCHO (Wittrock et al., 2006) enabled an improved assessment of atmospheric VOC levels and the knowledge of the ratio of CHO.CHO-to-HCHO (R_GF), (Vrekoussis et al., 2010), provides some source differentiation of source types. Studies have used HCHO, partly in combination with CHO.CHO to estimate the biogenic isoprene emissions (Fu et al., 2007; Stavrkou et al., 2009a, b, c; Liu et al., 2012; Marais et al., 2012). This is the largest natural source of CHO.CHO (Guenther et al., 2006; Fu et al., 2007). The amount of biogenically emitted VOC depends on several factors including, among others, the plant species and weather conditions (e.g. temperature and humidity) (Guenther et al., 2000). In industrialized areas, urban and rural regions, there are also contributions to the amounts of CHO.CHO from human activities, such as from fossil fuel production, distribution and combustion: the largest anthropogenic source of VOC precursors of CHO.CHO being
motor vehicle emissions due to either evaporation or incomplete combustion of fuel (Kansal, 2009). Globally, 55% of CHO.CHO is produced by biogenic precursors, while 27% are from anthropogenic and the remaining 18% from pyrogenic emissions, which include wildfires and biomass burning (Stavrakou et al., 2009a). Fires and vehicle exhausts are thought to be the only two sources, which directly emit CHO.CHO (Stavrakou et al., 2009a; Zhang et al., 2016).

In August 2018, unusually high temperatures caused severe drought in some areas of North America and resulted in the outbreak of many wildfires: the province of British Columbia (BC) in Canada was one of the most affected areas. The 2018 season has been the worst on record, with 6826 fires being detected and an area of approximately 22500 km² of land burned (Canada, 2018; Natural Resources Canada, 2018). These fires emitted many different species pollutants into the atmosphere, e.g. CO, NOx, VOC, OVOC, O₃, SO₂, CO₂, HCHO, HONO, CH₃CO₂O₂NO₂ (PAN) and other toxic species and aerosols (Urbanski et al., 2018). During the transport of plumes from fires, photochemical transformation of emitted species occurs. Overall, pollution resulting in low-polluted air quality is transported to those regions where the plumes descend to the surface. HCHO and are dispersed. CHO.CHO and HCHO column amounts are observed by remote sensing from satellite using Differential Optical Absorption Spectroscopy (DOAS), using measurements of the radiances backscattered from the Earth’s surface and atmosphere. The global maps of the HCHO and CHO.CHO and HCHO retrieved from SCIAMACHY, GOME-2, and OMI show enhanced HCHO over tropical rain forests but also over other regions with high isoprene emissions. In addition, hot-spots of HCHO, CHO.CHO and HCHO from fire emissions can be detected over large wildfires (Wittrock et al., 2006; Vrekoussis et al., 2009, 2010; Lerot et al., 2010; Chan Miller et al., 2014; Alvarado et al., 2014; De Smedt et al., 2008, 2012, 2015; Smedt et al., 2018).

In this study, we present novel observations of CHO.CHO and HCHO retrieved from the high spatial resolution observations of the instrument TROPOMI on board the S5P platform. On 7 August 2018, strongly elevated amounts of CHO.CHO and HCHO were observed over British Columbia and attributed to being predominantly from the fires. Surprisingly, these elevated levels of CHO.CHO and HCHO were not limited to the vicinity of the fires. The fire plumes, which contain both CHO.CHO and HCHO remain visible for several days and appear to travel long distances from the sources. We have used forward simulations of atmospheric transport of air masses calculated using the FLEXPART model (Pisso et al., 2019a), enable the investigation of long-range transport of CHO.CHO and HCHO during the studied period. FLEXPART simulations of a tracer (Pisso et al., 2019). The simulations include an effective first order loss, which determines the mean effective lifetime of the tracer. Those tracers emitted over the fire hot-spots and having with a lifetime of ≈29 hours can long effective lifetimes reproduce best the evolution of the plumes of CHO.CHO and HCHO for most of the fire events, and thus provide estimates of the effective lifetimes of CHO.CHO and HCHO in the plumes, as is described in the sections below. In addition, The RGF provides knowledge about their sources in the plume, CO and nitrogen dioxide, NO₂, have respectively longer and shorter lifetimes with respect to reaction with OH, and smoke and aerosol are also transported in the plumes from...
fires. Consequently the retrieved vertical column densities of carbon monoxide (CO) retrievals also CO and NO\textsubscript{2} from the TROPOMI instrument and true color images from VIIRS satellite instrument on NPP, which measures near simultaneously with TROPOMI are used as complementary information in order to interpret the apparent enhanced lifetime of CHO.CHO and HCHO in the plume. Additionally, interpretation of the main source of these species is performed by computing the ratio of CHOCHO to CHO.CHO and HCHO for in the specific events.

2 Methods

2.1 CHO.CHO and HCHO observations

The Differential Optical Absorption Spectroscopy (DOAS) method has been successfully applied to retrieve atmospheric columns of trace gases having fingerprint narrow absorption bands in the solar spectral range from space-borne instruments (e.g. Burrows et al., 1999). As noted above, there are several studies describing retrievals of OVOC and their use for the identification of VOC sources and their emissions (Burrows et al., 1999; Palmer et al., 2001; Wittrock et al., 2006; Kurosu et al., 2007; Vrekoussis et al., 2009, 2010; Lerot et al., 2010; De Smedt et al., 2008, 2012, 2015, 2018; Hewson et al., 2013; González Abad et al., 2015; Chan Miller et al., 2014; Alvarado et al., 2014, 2015). Algorithms for the retrieval of HCHO and CHO.CHO have been developed for measurements from the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) (Burrows et al., 1995; Bovensmann et al., 1999), the Ozone Monitoring Instrument (OMI) (Levett et al., 2006), and the second Global Ozone Monitoring Experiment on MetOp–A and –B (GOME2–A and–B) (Munro et al., 2016), which in combination provide a continuous dataset covering a period of more than 20 years. In this study, measurements from the TROPOMI instrument on board of the Sentinel–5 Precursor (Veefkind et al., 2012) are used to retrieve atmospheric column amounts of CHO.CHO and HCHO. A brief instrument description and relevant details of the retrieval of CHO.CHO and HCHO are given below.

2.2 The TROPOMI instrument

The TROPOspheric Monitoring Instrument (TROPOMI) onboard of the Copernicus Sentinel-5 Precursor satellite was launched on 13 October 2017. It has a spectral range in the UV-VIS-NIR-SWIR covering wavelengths from 270 to 500 nm in the UV- VIS, from 675 to 775 nm in the NIR and in a SWIR band from 2305 to 2385 nm. These bands allow the observation of several relevant atmospheric species, including CHO.CHO, HCHO, NO\textsubscript{2} and CO. TROPOMI provides nearly global coverage each day at a spatial resolution of currently which in August 2018 was 3.5 km×7 km (7 km×7 km in the SWIR). The equator crossing time is 13:00 LT (ascending node). Similar to OMI, TROPOMI is a nadir-viewing imaging spectrograph, which consists of employing a two-dimensional CCD, one dimension collecting the spectral information, the other being used for the spatial information. The TROPOMI instrument onboard of the S5P satellite provides data since November 2017 (Veefkind et al., 2012).
In recent years, several improvements on the retrieval of CHO.CHO have been reported. In 2014, Chan Miller et al. (2014) and Alvarado et al. (2014) presented new CHO.CHO retrieval algorithms applied to OMI measurements. These studies, similar to previous studies on GOME–2A data, introduced approaches to reduce interference by other absorbers, such as liquid water and nitrogen dioxide (NO$_2$). In this study, an optimized retrieval algorithm for CHO.CHO was developed, building on the heritage from the OMI CHO.CHO retrieval presented by Alvarado et al. (2014), extended and applied to S5P measurements. Previous studies have shown that cross-correlations between references cross-sections, as well as instrumental structures or features and shifts in the wavelength calibration can introduce systematic errors in the retrieval. As a result, a strong dependence on the fitting window was identified in the retrieved CHO.CHO slant column densities, SCDs (Chan Miller et al., 2014; Alvarado et al., 2014). In this study, a fitting window from 433 to 465 nm was chosen, which is slightly larger than windows used in previous investigations (Vrekoussis et al., 2010; Alvarado et al., 2014). This fitting window, which enables the liquid water absorption to be retrieved, leads to a reduction in the number of negative CHO.CHO SCDs over oceanic regions in comparison to a shorter fitting window (e.g. 434–458 nm), as well as a reduction in the residuals. The wavelength range selected covers the strong absorption bands of CHO.CHO (452-457 nm), which have already been used in the past to retrieve CHO.CHO from ground and ship-based DOAS configurations as well as from satellites (Sinreich et al., 2007, 2010; Wittrock et al., 2006; Vrekoussis et al., 2009, 2010; Lerot et al., 2010; Chan Miller et al., 2014; Alvarado et al., 2014). In order to optimize the quality of the retrievals, a row-dependent daily mean Pacific spectrum from the region 50°S, 160°E – 50°N, 135°W is used as a background spectrum (Alvarado, 2016), which is computed by averaging over the whole latitude range (50°S – 50°N) for each across-track viewing direction independently. In addition, the mean CHO.CHO SCD over the region 30°S, 150°W – 30°N, 150°E is computed each day and subtracted from all SCDs to correct for possible offsets. A summary of the selected absorption cross-sections, and other parameters used in the retrieval, as well as a list of the species included in the retrieval, is shown in Table 1.

SCDs depend on observation geometry. Vertical column densities (VCDs) are derived from the SCDs by use of so-called air mass factors (AMFs), which depend on the trace gas profile, air pressure, surface albedo, temperature, aerosols, clouds, and on solar zenith angle and measurement geometry. As the focus of this study is the observation of CHO.CHO in biomass burning emissions, a simple CHO.CHO profile with a Gaussian distribution having its maximum peak at the altitude of the aerosol layer is used (see Figure 1-A). This is based on the assumption that CHO.CHO is found at the same location as the main plume of aerosol and other trace gases. The altitude of the aerosol layer was estimated from profiles retrieved by the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) (Vaughan et al., 2004) (Figure 1-B). These aerosol extinction coefficients ($k_{ext}$) profiles retrieved at 532 nm are also used in the calculation of the AMFs by the radiative transfer model SCIATRAN (Rozanov et al., 2013). The computations have been performed on a daily basis, assuming a single scattering albedo of 0.92 and a homogenous distribution of aerosols characterized by the mean profile in the whole
region of study. The latter is computed from the average of all aerosol profiles, for every single latitude and longitude, and by taken over the region after removing cloud-contaminated pixels (see Figure 1-C). Clouds are not explicitly accounted for in the CHO.CHO and HCHO retrievals but data are filtered for the presence of clouds using an intensity criterion corresponding to a cloud radiance fraction of about 50%.

Table 1. Summary of retrieval parameters of CHO.CHO and HCHO de-from S5P with the respective absorption cross-sections used.

| Parameters          | Formaldehyde (HCHO) | Glyoxal (CHO.CHO) |
|---------------------|---------------------|-------------------|
| Fitting window      | 323.5-361 nm        | 433-465 nm        |
| Polynomial          | 5 coefficients      | 5 coefficients    |
| Cross-sections used |                     |                   |
| HCHO (Meller and Mootgat, 2000) | Yes (298 K) | No               |
| CHO.CHO (Volkamer et al., 2005) | No              | Yes (296 K)      |
| NO₂ (Vandaele et al., 1998) | Yes (220 K) | Yes (220K, 2294 K) |
| O₃ (Thalman et al., 2013) | Yes (293K) | Yes (293 K)      |
| O₃ (Serduchenko et al., 2014) | Yes (223 K, 243 K) | Yes (223 K) |
| BrO (Fleischmann et al., 2004) | Yes (223 K) | No               |
| H₂O (Rothman et al., 2013) | No              | Yes (296 K)      |
| Liquid water (Mason et al., 2016) | No             | Yes (280 K)      |
| Ring effect         | Ring cross section calculated by SCIATRAN model (Vountas et al., 1998) |
Non-linear ozone absorption effects, 2 pseudo absorption cross-sections \((O_3 \cdot \lambda + (O_3)^2)\) from Taylor expansion (Puķīte et al., 2010)

| Method                        | Applied  |
|-------------------------------|----------|
| Iterative spike removal       | Yes      |
| Intensity offset correction   | No       |
| Background spectrum           | No       |

**Figure 1.** A) CHO.CHO and HCHO profiles assumed in the computation of AMFs. B) CALIPSO average profile of aerosol extinction coefficients \((k_{ext})\), averaged over for all latitudes and longitudes of Figure 1-C, excluding cloudy scenes. C) Top panel: Example of CALIPSO Aerosol profile extinction coefficients retrieved at a wavelength of 532 nm. Aerosol and cloud optical depth are shown as a function of latitude and longitude for every single profile. Bottom panel: Colour coded \(k_{ext}\) for every latitude and longitude in the selected region. Purple spots represent cloudy scenes. The black line depicts the aerosol layer height.

### 2.4 HCHO retrieval from TROPOMI measurements

The accuracy of DOAS retrievals of HCHO is limited by cross-correlations with strong absorbers in the UV (e.g. O\(_3\)) and the signal to noise ratio of the radiance spectra measured by the instrument. Here, an updated and optimized version of the formaldehyde retrieval developed by Wittrock et al. (2006) and Vrekoussis et al. (2010) is used, which applies a slightly larger fitting window extending from 323.5 nm to 361 nm, resulting in a reduction in the noise of the retrieved slant columns, column densities. At wavelengths shorter than 336 nm, interference with O\(_3\) is observed due to the strong absorption of the latter. HCHO, which is about three orders of magnitude smaller. This effect is compensated by applying the method described by Puķīte et al. (2010), which consists of adding two additional pseudo-cross-sections to the fit (\(\lambda \sigma_{O_3}\) and \(\sigma_{O_3}^2\)) (Puķīte et al., 2010; De Smedt et al., 2008, 2015, 2015; Smedt et al., 2018).
The cross-sections of interfering species are included in the fit as listed in Table 1. In a manner similar to glyoxal, the retrieval of CHO.CHO, a synthetic ring spectrum (Vountas et al., 1998) is used to account for the Ring effect and a row-dependent daily mean Pacific spectrum from the region 50°S, 135°W – 50°N, 160°E is used as background spectrum. Also, a latitude dependent offset correction based on SCDs from longitudes between 180° E and 160° E is applied to the data. As for CHO.CHO, VCDs are computed using AMFs, assuming a Gaussian shape for the distribution of HCHO at the layer where the aerosols are located— *in the plume*. Figures 2-A and 2-B show examples of CHO.CHO and HCHO fit results for the 10th of August 2018, compared to the differential reference cross-section for a single measurement. For an individual CHO.CHO measurement, the detection limit is of the order of $5 \times 10^{14}$ molec.cm$^{-2}$, which is about 10 times smaller than the columns detected from emissions of the wildfires over the British Columbia region of Canada. For HCHO, the detection limit is an order of magnitude higher ($5.45 \times 10^{15}$ molec.cm$^{-2}$). The detection limit of a single S5P measurement in this study has been estimated in a manner similar to that explained in Alvarado et al. (2004).

Figure 2. A) Example fit for CHO.CHO from a single measurement of S5P taken at latitude 53.0° and longitude 125.6°W, on the 10th of August 2018 and for a solar zenith angle of 39.3°. B) Example fit for HCHO from a single measurement of S5P taken at latitude 59.1° and longitude 109.0° W, on the 10th of August 2018 and for a solar zenith angle of 44.6°. The black line depicts the scaled differential cross-section and the red line the fit. The SCD values for this example are $9.3 \times 10^{15}$ molec.cm$^{-2}$ for CHO.CHO and $4.6 \times 10^{16}$ molec.cm$^{-2}$ for HCHO, respectively. The detection limit for a single measurement from S5P is estimated to be $5.0 \times 10^{14}$ molec.cm$^{-2}$ and $5.45 \times 10^{15}$ molec.cm$^{-2}$ for CHO.CHO and HCHO, respectively.
2.5 Simulation of tracer transport with FLEXPART

In order to simulate the transport of emissions from the Canadian wildfires, forward simulations with version 10.3 of the FLEXible PARTicle dispersion model FLEXPART (Stohl et al., 2005; Pisso et al., 2019) have been performed. The model was driven by using hourly wind fields from the ECMWF ERA5 reanalysis (C3S) at 0.25° horizontal resolution. As a transport model, FLEXPART cannot adequately simulate the complete set of chemical transformations leading to the observed lifetimes of trace gases in the biomass burning plumes. Nevertheless, performing simulations for tracers having different mean lifetimes and comparing these to the observed columns yields a valuable insight into the effective lifetime, which the emitted substances have to have in the plume. Performing simulations for tracers having different mean lifetimes and comparing these to the observed columns yields a valuable insight into the effective lifetime, which the emitted substances have to have in the plume. An effective mean lifetime can be estimated by comparing the observed behaviour of the CHO, CHO and HCHO with different FLEXPART simulations of different assumed tracer lifetimes.

In FLEXPART, the mean-effective mean lifetime $\tau$ of an emitted tracer is treated as exponential decay with a given half-life ($t_{0.5}$); $\tau$ can then be calculated according to $\tau = t_{0.5}/\ln(2)$. As part of this study, FLEXPART simulations were carried out with half-life times of 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 hours, corresponding to effective mean lifetimes of $\sim$2.9, 5.8, 8.7, 11.5, 14.4, 17.3, 20.2, 23.1, 26.0, and 28.9 hours, respectively. As the exact emissions rates from the wildfires are highly uncertain, the emission fluxes from the Canadian wildfires are assumed to be proportional to fire radiative power (FRP, see below for more details). This means that effectively, emissions are prescribed in the model in arbitrary mass units; scaling the individual emission sources with FRP ensures that when aggregating the simulation results from all fires, each fire’s relative contribution to the simulated columns is retained, and the results can be compared to the observed columns. The emissions, prescribed in the model, are taken from the Global Fire Assimilation System (GFAS) daily FRP and plume height data (Rémy et al., 2017). Simulations were performed on a daily basis for the period 6 August to 23 August 2018. For each day, all fires from the GFAS data, which had an FRP of more than 3 W/cm$^2$ were gridded to a 0.350° horizontal pattern. The model was then run forward in time for 120 hours, releasing the tracer for the first 24 hours (the full UTC day) from each of the 0.350° grid cells, assuming no temporal variation throughout the day. Vertically, the emissions within the grid cells were evenly distributed over the range of mean altitude of maximum injection heights given by the GFAS data for the respective grid cell. The output of the simulation contains gridded mass concentrations for each time step. Here, a grid with a horizontal resolution of 0.03125° was chosen, to match the resolution of the gridded satellite observations. Hourly output from the simulation was recorded and then vertically integrated to yield simulated tracer columns. In a post-processing step, for one specific mean lifetime, all simulation results (i.e., simulations for all fires on all days) were aggregated into one dataset. While the absolute tracer column density from the model output cannot be simply compared to the measurements, a comparison of the plume patterns and relative distribution between satellite observation and model output gives an indication about the meaningfulness of the prescribed mean lifetime. At this point, the aggregated model output for one effective mean...
lifetime consists of hourly latitude-longitude grids of vertical tracer columns throughout the whole study period. For comparison to the satellite observations, the hourly time slice closest to the time of overpass at 53°N was chosen.

3 Results and discussion

During August 2018, a high-temperature anomaly led to the outbreak of many fires in the Canadian Western province of British Columbia, resulting in the emission of large quantities of particles and traces gases that in turn affected air quality in the region. As shown in Figure 3-A and -B, the monthly average of CHO.CHO and HCHO vertical columns from S5P show strongly enhanced values over the fire region, suggesting that these fires were a large direct and/or indirect source of CHO.CHO and HCHO. Surprisingly, the CHO.CHO and HCHO enhancements are not limited to the main fire region but extend over large parts of Canada, where only a few fires were observed. In order to investigate the sources of CHO.CHO and HCHO and their distributions, 24-hour assimilation data of fire radiative power from the Global Fire Assimilation System (Kaiser et al., 2012) are analysed. Briefly, FRP is a measure of outgoing radiant heat from fires, measured in units of W.cm\(^{-2}\) and retrieved from space by the MODe rate resolution Imaging Spectroradiometers (MODIS) on board of Terra and Aqua satellites (Justice et al., 2002). The assimilated FRP spatially aggregates all valid fire and non-fire observations from both MODIS instruments onto a horizontal resolution of 0.1° x 0.1° and computes the total FRP sums for each grid bin (Justice et al., 2002). The FRP is also used as input in the FLEXPART simulation as described in section 2.5 as a proxy for emission strength. Figure 3-C shows a monthly average FRP map over North America for August 2018.

![Figure 3. Monthly average of CHO.CHO (panel A) and HCHO (panel B) VCDs retrieved from the TROPOMI instrument on S5P for August 2018, and over North America (A and B). Panel C shows the integrated FRP from MODIS for the same period.](image-url)
The highest CHO.CHO VCD values are found over the locations of the most intense fires, as intuitively expected. The HCHO distribution over the fire regions is similar to that of CHO.CHO, but with some differences in the relative distribution. In addition, enhanced CHO.CHO and HCHO columns are also apparent over the southeastern US, where large isoprene emissions occur. CHO.CHO and HCHO are also detected in plumes crossing central and eastern Canada, where no fires are identified in the FRP map. This pattern points to the transport of CHO.CHO and HCHO emanating from the wildfires. However, it is well known that CHO.CHO and HCHO have been reported to have short atmospheric lifetimes of about ~2.2 and ~4.0 hours during daytime, respectively (Atkinson, 1998; Volkamer et al., 2005a). Assuming that the lifetime in the plume is not sufficient to explain the observed pattern at the ground, we expect that CHO.CHO would be removed reasonably close to the fire sources. HCHO would be transported further but we would also expect that it would be transported no more than approximately twice as far as CHO.CHO.

Earlier studies by Wittrock et al. (2006) and Vrekoussis et al. (2009, 2010) showed that CHO.CHO is also observed over oceanic regions, where no CHO.CHO source is expected. The potential of a) a long-range transport of CHO.CHO and/or of CHO.CHO precursors from continental areas, and b) having an unknown oceanic CHO.CHO source were discussed as a possible explanation in part of these observations, but no firm conclusions could be drawn so far. In the present study, with the support of the simulations using FLEXPART model, evidence of long-range transport of CHO.CHO and HCHO or its precursors from biomass burning emissions is shown investigated. In order to further investigate this context the transport of CHO.CHO and HCHO during two fire plume episodes form different periods of satellite measurements are selected (07-10 and 20-21 of August 2018) and are discussed below.

3.1 CHO.CHO and HCHO emissions from the British Columbia wildfires: 07-10 and 20-21 August 2018

Figure 4-A shows daily maps of CHO.CHO and HCHO VCDs over Canada for the period 7th to 10th of August 2018. The most intense wildfires are found on the 7th of August 2018 and remain detectable until the 10th of August. The location of those fires corresponds well to the location, where both trace species are detected on the first day of the fire. The CHO.CHO and HCHO distributions are changing then change from day to day. However, a large plume is formed clearly visible on the 10th of August 2018. Enhanced CHO.CHO and HCHO columns are found at a distance of up to ~1500 km from the fires, indicating transport over long distances.

To investigate possible transport pathways, forward simulations of the atmospheric transport with FLEXPART were calculated for the same period as HCHO and when CHO.CHO observations and HCHO plumes are observed (see Figure 4-B), assuming a random effective lifetime of 14.4 hours. The latter is in contrast to the significantly longer than lifetimes of CHO.CHO and HCHO expected, which are significantly shorter, found in the literature. On the other hand, the simulated pattern of air masses follows the distribution of same distinctive path as CHO.CHO and HCHO columns well.
showing VCDs. This shows good spatial agreement between simulations and satellite observations. The tracer simulated with FLEXPART spreads over the same area as CHO.CHO, providing evidence for the transport of CHO.CHO and HCHO and their precursors over continental Canada. This is even more evident for the second period of interest in this study, which extends from the 20th to 21st of August 2018 (see Figure 7). While the spatial match of plume and model is good in this example, it is clear from the figure that even an effective lifetime of 14.4 hours does not describe fully the extent of the trace gas transport, CHO.CHO and using HCHO transported. Using shorter effective lifetimes for CHO.CHO and HCHO, taken from the literature would not reproduce the observations, however. However both lifetimes depend on time of day (daytime and nighttime) and also on photon flux conditions in the plume: on the diurnal photolysis and OH diurnal pattern cycles as well as on wet/dry deposition processes and other oxidants. Consequently, comparisons of FLEXPART simulations with different effective lifetimes were performed for two selected days, which are detail discussed as is shown in Section 3.2.

![Figure 4. A) and B) Daily CHO.CHO and HCHO VCDs retrieved from S5P measurements for the period 7 to 10 of August 2018. C) Distribution of a tracer with a lifetime of 14.4 hours simulated with FLEXPART for the same period. The CHO.CHO in the plume decreases on average from $3 \times 10^{15}$ molec.cm$^{-2}$ to $3 \times 10^{14}$ molec.cm$^{-2}$, while the HCHO has a different variation into the plume but at the end of the plume, it decreases from $34 \times 10^{16}$ molec.cm$^{-2}$ to $21 \times 10^{16}$ molec.cm$^{-2}$. The FLEXPART tracer column decreases from $3 \times 10^6$ to $0.3 \times 10^6$ for this specific effective lifetime of 14.4 hours.]

3.2 **Effective Lifetimes of CHO.CHO and HCHO in the Plume**

Figure 5 shows the results of FLEXPART simulations assuming effective lifetimes for a surrogate chemical species of ~2.9, 14.4, 23.1, and 28.9 hours for the 10th and 20th of August 2018. From this figure, it is clear that only for the simulations having effective lifetimes of 23.1 hours or more, a significant fraction of the tracer emitted is present at the end...
of the plume as observed in the measurements. This is further also illustrated in Figure 6, depicting CHO.CHO and HCHO maps for the 10th of August 2018. On top of these maps, contour lines are shown for the simulated air masses assuming effective lifetimes of 2.9, 14.4, and 28.9 hours. It is evident that in both cases the tracer distributions simulated with longer effective lifetimes better describe the observed distribution of glyoxal CHO.CHO and formaldehyde HCHO.

Figures 7-A, -B, -C present a second comparison of daily maps of glyoxal CHO.CHO and formaldehyde HCHO VCDs with a FLEXPART tracer having an effective lifetime of 28.9 hours for the period for 20th and 21st of August 2018. It is evident that again, the tracer follows the distribution of CHO.CHO and HCHO observations, similar to the first period studied (see Figure 4). However, on 20th and 21st of August 2018, the CHO.CHO plume spreads and HCHO plumes spread over the ocean, where no glyoxal or formaldehyde sources are expected, until it disperses after being transported over a distance of about 600 km from the fires.
The observed behaviour of the CHO.CHO and HCHO plumes is in contrast with the short atmospheric lifetimes resulting from their rapid removal by photolysis and reaction with OH. In addition, CHO.CHO oligomerises and thus is a source of SOA formation (Schweitzer et al., 1998; Jang et al., 2002; Liggio et al., 2005; Kroll et al., 2005; Loeffler et al., 2006; Volkamer et al., 2007; Fu et al., 2007; Myriokefalitakis et al., 2008; Stavrakou et al., 2009b, c). The simplest explanation of the observations of CHO.CHO and HCHO is that, during the fire events, both species are transported and/or produced during
transport over long distances, resulting in an effective lifetime of about 28.9 hours. This would imply the transport of the VOC precursors of CHO.CHO and HCHO.

![Comparison with model lifetimes - CHOCHO: 10 Aug. 2018](image)
![Comparison with model lifetimes - HCHO: 10 Aug. 2018](image)

**Figure 6.** Daily maps CHO.CHO and HCHO VCD retrieved from S5P for 10th of August 2018 compared with FLEXPART tracer simulations having three different lifetimes (∼2.9, 14.4, and 28.9 hours).

One reason for the large dispersion of the CHO.CHO and HCHO plumes is the injection of the biomass burning emissions into the free troposphere, where high wind speeds favour transport over long distances. This is a well-known effect that has also been observed for NO$_2$ in GOME-2 data (Zien et al., 2014). However, even at high wind speeds, the short lifetime of these species would result in much smaller dispersed plumes than the ones observed. There are three possible explanations for this apparent contradiction:

**Reason 1:** The lifetimes of CHO.CHO and HCHO could be significantly longer than expected in these biomass burning plumes. If the OH mixing ratio and UV and visible radiation within the plume are much lower than outside the plume. There is, however, no indication that this should be the case; on the contrary, OH levels in the biomass burning plume are expected to be enhanced (Folkins et al., 1997), leading to a reduction of the expected CHO.CHO lifetime in the unpolluted troposphere. Folkins et al., 1997, leading to a reduction of the expected CHO.CHO and HCHO lifetimes. In this context, it is interesting to investigate the NO$_2$ VCD observed. The NO$_2$ plumes coming from the biomass burning are shown in figure 8-B. During daytime NO$_2$ is removed in the gas phase by reaction with OH. Provided sufficient O$_3$ is present the photolysis of NO$_2$ produces NO and O which react respectively with O$_3$ to make NO$_2$ and oxygen molecules to make O$_3$. This is known as a “do nothing cycle”. NO$_2$ appears to decay relatively rapidly in the plumes coming from the fires. Our assumption that oxidation and photolysis of CHO.CHO and HCHO is relatively rapid, is thus not contradicted by the NO$_2$ decay in the fire plumes.
Reason 2: There could be an efficient recycling process between the gas and aerosol phase, resulting in the observed extended effective lifetimes of CHO.CHO and HCHO. However, this reason is considered unlikely, because there is not yet any strong evidence of HCHO being a precursor of SOA formation, and as the shape of the plumes for both trace gases is similar, a similar mechanism is expected for both. Also, evidence for the release of CHO.CHO following the formation of oligomers in the aerosol phase, is limited (Kroll et al., 2005, and references therein).

![Images of CHO.CHO and HCHO VCDs retrieved from S5P measurements for the period from 20 to 21 of August 2018. C) Tracer distribution simulated with FLEXPART for the same period assuming a lifetime of 28.9 hours. Enhanced CHO.CHO columns spread over the ocean in a pattern similar to that simulated by the model tracer.]

Reason 3: The plume could contain glyoxal CHO.CHO and formaldehyde HCHO precursors, i.e. VOCs, which are slowly oxidized, releasing CHO.CHO and HCHO along the trajectory, resulting in an apparent increase in lifetime. In order to better assess the CHO.CHO and HCHO spatial distribution seen on the 10th of August 2018, two additional S5P TROPOMI retrievals have been taken into account; the column-averaged dry air mole fractions of CO, retrieved by the algorithm described in Schneising et al. (2019), and the VCD NO₂ VCD retrieved using an algorithm similar to the one described for the GOME-2 instrument (Richter et al., 2011) and using AMF calculated following the same approach as the one described before for glyoxal CHO.CHO and formaldehyde HCHO (see section 2.3). The CO plume shows a similar spatial behavior as HCHO pattern to those of CHO.CHO and CHO.CHO-HCHO (see Figure 8-E). As CO is a relatively long-lived tracer of fire emissions, having a lifetime with respect to OH of months, this is further confirmation for the fact that supports the fire origin of the VOCs and/or their precursors originate from the fires and then undergo long-range transport. As noted above, NO₂ is removed by OH faster than CHO.CHO and HCHO. The NO₂...
VCD enhancements, in contrast to those of CHO.CHO and HCHO, are limited to the proximity of the fire hot-spots (see Figure 8-D). This is the behaviour expected for a molecule with a short atmospheric lifetime and highlights how unusual the behavior of the VOCs is. A true-colour image from the Visible Infrared Imaging Radiometer Suite (VIIRS) clearly shows the distribution of smoke and aerosols produced because of the emission from the fires being transported and transformed (Figure 8-F). The distribution of the aerosol appears qualitatively to be similar to the CHO.CHO, HCHO, and CO distributions, indicating that species in the transported plumes are mixed in the aerosol layer. Mixtures of CO, CHO.CHO, HCHO, aerosol and presumably other pollutants released by the fire. It is interesting to note that CHO.CHO and CO follow mainly the main plume, while the HCHO distribution is more diffuse and shows enhanced values also over regions where a thinner aerosol plume is visible in the VIIRS image. This may possibly originate from another unidentified fire as this part of the plume or another unknown source, which is not included in the our FLEXPART simulations.

As an additional criterion, the ratio of CHO.CHO - to - HCHO formaldehyde (RGF) is shown in Figure 8-C. Larger values of RGF are found close to the location of the wildfires as already reported in previous publications (Vrekoussis et al., 2010). This is an indication of enhanced primary emissions of glyoxal relative to those of HCHO from fires. Progressively lower RGF values are then found until the end of the plume suggesting either a decreasing of glyoxal production over time or a change of CHO.CHO relative to that for HCHO during the transport of polluted air in the fire emissions injected into the plume. Another potential explanation would be the mixing in of air from different origins, having lower CHO.CHO and/or higher HCHO different concentrations of the trace gases, during the plume transport. This is however not confirmed by the observed CO behaviour, which shows a similar spatial distribution to CHO.CHO and HCHO.

The comparison of retrieved S5P columns and FLEXPART tracer simulations discussed is based on a number of simplifications. First of all, the observational conditions of the biomass burning plumes are complex, and aerosol scattering and absorption certainly impact on the sensitivity of the retrievals. While this is taken into account by using air mass factors for elevated plumes positioned at altitudes derived from CALIPSO observations, there remains considerable uncertainty with respect to absolute values. Aerosol loading and optical properties will vary along the plume and thus will the retrieval sensitivities, and this is not modelled here explicitly in this study. However, the differences apparent between the spatial distributions of glyoxal CHO.CHO and NO2, which are retrieved in very similar spectral regions, provide evidence for the fact that measurement sensitivity is does not explain the driver for differences in the observed VCD plume patterns. Another crucial simplification is the assumption of a constant fire emissions and the proportionality of FRP and emission strength in the FLEXPART simulations. In reality, fire emissions will also depend on the type of biomass burned, the age of the fire, the time of the day and the environmental conditions, and this will have an effect on the trace gas distribution along the plume, which reflects both chemical transformation and the history of emissions. Modelling of this
time-evolution is complex, if possible at all, and out of the scope of this study. However, the observation that both CHO.CHO and HCHO are present in the biomass burning plume after extended time periods and over long distances is robust and can only be explained by continuous release of CHO.CHO and HCHO from the transformation of longer-lived precursors and/or efficient recycling processes in the plume as discussed above.

Figure 8. Panels A, B, D, and E show the CHO.CHO, HCHO, NO$_2$, and CO columns, respectively retrieved from S5P measurements for 10th of August 2018. Note that CO columns are unfiltered and only represent a qualitative description of the plume. The AMFs used for CHO.CHO, HCHO, and NO$_2$ are appropriate for the biomass burning plume only. Panel C depicts the calculated CHO.CHO-to-HCHO (R$_{GF}$) for the same day. Panel F shows a true colour image of the aerosol distribution from VIIRS for 10th of August 2018.

4 Summary and conclusions

The retrieval of formaldehyde and glyoxal total column amounts CHO.CHO and HCHO VCDs from measurements of the TROPOMI instrument on board the Sentinel-5P satellite is reported. This enables the extension of the datasets already available from the SCIAMACHY, GOME-2, and OMI instruments, and shows the advantage of the high spatial
resolution and low noise of TROPOMI for studying specific geophysical phenomena. The is well demonstrated in the features and plumes seen in the CHO.CHO, HCHO, CO, and NO₂ VCDs.

In this case study the satellite data show clear evidence for pyrogenic emissions of CHO.CHO and HCHO—and their precursors during the wildfire season in summer 2018 in British Columbia, Canada. The spatial and temporal pattern of the highest retrieved CHO.CHO and HCHO columns are associated with areas having high fire radiative power, as observed in the MODIS fire data products, indicating. This indicates that in these areas, pyrogenic emissions are the dominant source of CHO.CHO and HCHO. In addition to local enhancements of NO₂, CHO.CHO, and HCHO, close to the fires, extended plumes of elevated CHO.CHO and HCHO amounts are observed on some days downwind of the fires. This finding provides evidence of either a) long-range transported VOCs, primarily emitted from the fires or b) their production from precursor species during the transport of NO₂, which is also transported but is short lived. The spatial and temporal VOC CHO.CHO and HCHO distribution observed from satellite follows the same pattern as to that of CO, which is long lived, and that simulated by the FLEXPART dispersion model, initialized by tracer emissions starting at known fire locations. Enhanced CHO.CHO and HCHO columns were found in the S5P data up to 1500 km from their sources.

In order to obtain reasonable agreement between the model results and the measurements, an effective tracer lifetime of more than 20 hours and up to 28.9 hours needs to be assumed in the FLEXPART simulations. This is significantly longer than the anticipated lifetimes of glyoxal CHO.CHO and formaldehyde HCHO. The long transport of glyoxal CHO.CHO and formaldehyde in HCHO along the length of the plume could be associated with the lifting of glyoxal and formaldehyde these traces gases being lifted from the boundary layer into the free troposphere, where high wind speeds lead to rapid transport.

The long apparent lifetime of CHO.CHO and HCHO in the transported plumes could either be explained by a real increase in atmospheric lifetime due to the specific plume because of photochemical conditions in the biomass burning plume or as we attribute, the presence of longer-lived precursors, which are oxidized to form CHO.CHO and HCHO during transport we consider unexpected. Based on our current knowledge, the most probable explanation of the apparent long lifetime of CHO.CHO and HCHO would be the latter where formation of glyoxal and formaldehyde within the plume is caused by the oxidation of a mixture of longer-lived emitted VOC species precursors, (e.g. methanol, ethanol, acetylene, aromatics, glycolaldehyde, ethylene etc.), that in turn, form CHO.CHO and HCHO—at different rates. Further research is needed to investigate how frequent such fire-related long-range transport events of VOCs are, what the exact chemical mechanism of the formation is and how of the CHO.CHO and HCHO in the plumes downwind of the fires needs to be identified. The assessment of the number of such fires events impact on ozone and their relevance for tropospheric O₃ and aerosol production downwind of the fires is required.
Author contributions. L. M. A. Alvarado, A. Richter and J. P. Burrows have prepared the manuscript with the contribution of all authors and developed the glyoxal and formaldehyde and NO$_2$ retrievals for TROPOMI measurements. M. Vrekoussis, A. Hilboll and A. B. Kalisz Hedegaard have designed and performed the FLEXPART experiment for simulations of the airmasses assuming different effective lifetimes. O. Schneising has developed the CO retrieval and provided the CO data for the comparison with glyoxal and formaldehyde products.

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Unexpected long-range transport of glyoxal and formaldehyde observed from the Copernicus Sentinel-5 Precursor satellite during the 2018 Canadian wildfires

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Abstract. Glyoxal (CHO.CHO) and formaldehyde (HCHO) are intermediate products in the tropospheric oxidation of the majority of Volatile Organic Compounds (VOC). CHO.CHO is also a precursor of secondary organic aerosol (SOA) in the atmosphere. CHO.CHO and HCHO are released from biogenic, anthropogenic, and pyrogenic sources. CHO.CHO and HCHO tropospheric lifetimes are typically considered to be short during the daytime at mid-latitudes (e.g. several hours), as they are rapidly removed from the atmosphere by their photolysis, oxidation by OH, and uptake on particles or deposition. At night and at high latitudes, tropospheric lifetimes increase to many hours or even days. Previous studies demonstrated that CHO.CHO and HCHO vertical column densities, VCDs, are well retrieved from space-borne observations using the differential optical absorption spectroscopy, DOAS. In this study, we present CHO.CHO and HCHO VCDs retrieved from measurements of the TROPOMI instrument, launched on the Sentinel-5 Precursor (S5P) platform in October 2017. We observe strongly elevated amounts of CHO.CHO and HCHO during the 2018 fire season in British Columbia, Canada, where a large number of fires occurred in August. CHO.CHO and HCHO plumes from individual fire hot-spots are observed in air masses travelling over distances of up to 1500 km, i.e. much longer than expected for the relatively short tropospheric lifetime expected for CHO.CHO and HCHO. Comparison with simulations by the particle dispersion model FLEXPART indicates that effective lifetimes of 20 hours and more are needed to explain the observations of CHO.CHO and HCHO if they decay in an effective first order process. FLEXPART used in the study calculates accurately the transport. In addition an exponential decay, in our case assumed to be photochemical, of a species along the trajectory is added. We have used this simple approach to test our assumption that the CHO.CHO and HCHO are created in the fires and then decay at a constant rate in the plume, as it is transported. This is clearly not the case and we infer that CHOCHO and HCHO are either efficiently recycled during transport, or continuously formed from the oxidation of longer-lived precursors present in the plume, or possibly a mixture of both. We consider the best explanation of the observed CHO.CHO and HCHO VCD in the
plumes of the fire is that they are produced by oxidation of longer-lived precursors, also released by the fire and present in the plume.

1 Introduction

Formaldehyde (HCHO) is produced in the oxidation of both methane (CH₄) and other Volatile Organic Compounds (VOC).

Glyoxal (CHO.CHO) is the smallest alpha-dicarbonyl formed in the oxidation of many VOC containing two or more carbon atoms. Although both CHO.CHO and HCHO, which are known as OVOC (Oxygenated Volatile Organic Compounds) have similar rates of reaction with the hydroxyl radical (OH) in the troposphere, the photolysis frequency of HCHO, which absorbs and is photolysed in the ultraviolet-A (UV-A), is significantly smaller than that of CHO.CHO, which absorbs in the blue. As a result, the atmospheric lifetime of HCHO is longer than that of CHO.CHO (Atkinson, 2000). Both species are short-lived during daytime due to their rapid removal by photolysis and reaction with OH radicals (Atkinson, 2000; Volkamer et al., 2007). These processes are the major sinks of CHO.CHO and HCHO, contributing about 69% and 96%, respectively. The remaining part of HCHO is removed by deposition (4%), while for CHO.CHO, 22% are removed by SOA formation and 8% by deposition (Stavrakou et al., 2009a, c). Additionally, HCHO and probably also CHO.CHO during the night are removed by reaction with nitrate (NO₃) radicals (Atkinson, 2000). CHO.CHO and HCHO play a key role in tropospheric chemistry because they act as temporary reservoirs releasing carbon monoxide (CO) and HOx (OH and Hydroperoxyl, HO₂) free radicals, which participate in catalytic cycles creating and destroying tropospheric ozone (O₃).

The slant and vertical column densities of HCHO were first observed from space using measurements from the GOME instrument (e.g. Burrows et al., 1999, and references therein). These columns were later used to estimate the emission strength of precursor VOC (Palmer et al., 2003; Abbot et al., 2003). The simultaneous observation of CHO.CHO and HCHO (Wittrock et al., 2006) enabled an improved assessment of atmospheric VOC levels and the knowledge of the ratio of CHO.CHO-to-HCHO (R_GF), (Vrekoussis et al., 2010), provides some differentiation of source types. Studies have used HCHO, partly in combination with CHO.CHO to estimate the biogenic isoprene emissions (Fu et al., 2007; Stavrakou et al., 2009a, b, c; Liu et al., 2012; Marais et al., 2012). This is the largest natural source of CHO.CHO (Guenther et al., 2006; Fu et al., 2007). The amount of biogenically emitted VOC depends on several factors including, amongst others, the plant species and weather conditions (e.g. temperature and humidity) (Guenther et al., 2000). In urban and rural regions, there are also contributions to the amounts of CHO.CHO from human activities, such as from fossil fuel production, distribution and combustion: the largest anthropogenic source of VOC precursors of CHO.CHO being motor vehicle emissions due to either evaporation or incomplete combustion of fuel (Kansal, 2009). Globally, 55% of CHO.CHO is produced by biogenic precursors, while 27% are from anthropogenic and the remaining 18% from pyrogenic emissions (Stavrakou et al., 2009a). Fires and vehicle exhausts are thought to be the only two sources, which directly emit CHO.CHO (Stavrakou et al., 2009a; Zhang et al., 2016).
In August 2018, unusually high temperatures caused severe drought in some areas of North America and resulted in the outbreak of many wildfires: the province of British Columbia (BC) in Canada was one of the most affected areas. The 2018 season is the worst on record, with 6826 fires being detected and an area of approximately 22500 km² of land burned (Natural Resources Canada, 2018). These fires emitted many different pollutants into the atmosphere, e.g. CO, NOx, VOC, OVOC, O₃, SO₂, CO₂, HCHO, HONO, CH₃CO.O₂.NO₂ (PAN) and other toxic species as well as aerosols (Urbanski et al., 2018). During the transport of plumes from fires, photochemical transformation of emitted species occurs. Overall, polluted air is transported to regions where the plumes are dispersed. CHO.CHO and HCHO column amounts are observed by remote sensing from satellite using Differential Optical Absorption Spectroscopy (DOAS) on measurements of the radiances backscattered from the Earth’s surface and atmosphere. The global maps of CHO.CHO and HCHO retrieved from SCIAMACHY, GOME-2, and OMI show enhanced CHO.CHO and HCHO over tropical rain forests but also over other regions with high isoprene emissions. In addition, hot-spots of CHO.CHO and HCHO from fire emissions can be detected over large wildfires (Wittrock et al., 2006; Vrekoussis et al., 2009, 2010; Lerot et al., 2010; Chan Miller et al., 2014; Alvarado et al., 2014; De Smedt et al., 2008, 2012, 2015, 2018).

In this study, we present novel observations of CHO.CHO and HCHO retrieved from the high spatial resolution observations of the instrument TROPOMI on board the S5P platform. On 7 August 2018, strongly elevated amounts of CHO.CHO and HCHO were observed over British Columbia and attributed to being predominantly from fires. Surprisingly, these elevated levels of CHO.CHO and HCHO were not limited to the vicinity of the fires. The fire plumes, which contain both CHO.CHO and HCHO remain visible for several days and appear to travel long distances from the sources. We have used forward simulations of atmospheric transport of air masses calculated using the FLEXPART model (Pisso et al., 2019). The simulations include an effective first order loss, which determines the mean effective lifetime of the tracer. Those tracers emitted over the fire hot-spots with long effective lifetimes reproduce best the evolution of the plumes of CHO.CHO and HCHO for most of the fire events, and thus provide estimates of the effective lifetimes of CHO.CHO and HCHO in the plumes, as is described in the sections below. The RGF provides knowledge about their sources in the plume. CO and nitrogen dioxide, NO₂, have respectively longer and shorter lifetimes with respect to reaction with OH, and smoke and aerosol are also transported in the plumes from fires. Consequently the retrieved vertical column densities of CO and NO₂ from the TROPOMI instrument and true color images from VIIRS instrument on NPP, which measures near simultaneously with TROPOMI are used as complementary information in our interpretation of the apparent enhanced lifetime of CHO.CHO and HCHO in the plume.
2 Methods

2.1 CHO.CHO and HCHO observations

The Differential Optical Absorption Spectroscopy (DOAS) method has been successfully applied to retrieve atmospheric columns of trace gases having fingerprint narrow absorption bands in the solar spectral range from space-borne instruments (e.g. Burrows et al., 1999). As noted above, there are several studies describing retrievals of OVOC and their use for the identification of VOC sources and their emissions (Burrows et al., 1999; Palmer et al., 2001; Wittrock et al., 2006; Kurosu et al., 2007; Vrekoussis et al., 2009, 2010; Lerot et al., 2010; De Smedt et al., 2008, 2012, 2015, 2018; Hewson et al., 2013; González Abad et al., 2015; Chan Miller et al., 2014; Alvarado et al., 2014, 2015). Algorithms for the retrieval of HCHO and CHO.CHO have been developed for measurements from the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) (Burrows et al., 1995; Bovensmann et al., 1999), the Ozone Monitoring Instrument (OMI) (Levelt et al., 2006), and the second Global Ozone Monitoring Experiment on MetOp–A and –B (GOME2–A and–B) (Munro et al., 2016), which in combination provide a continuous dataset covering a period of more than 20 years. In this study, measurements from the TROPOMI instrument on board the Sentinel-5 Precursor (Veefkind et al., 2012) are used to retrieve atmospheric column amounts of CHO.CHO and HCHO. A brief instrument description and relevant details of the retrieval of CHO.CHO and HCHO are given below.

2.2 The TROPOMI instrument

The TROPOspheric Monitoring Instrument (TROPOMI) onboard the Copernicus Sentinel-5 Precursor satellite was launched on 13 October 2017. It has a spectral range in the UV-VIS-NIR-SWIR covering wavelengths from 270 to 500 nm in the UV-VIS, from 675 to 775 nm in the NIR and in a SWIR band from 2305 to 2385 nm. These bands allow the observation of several relevant atmospheric species, including CHO.CHO, HCHO, NO$_2$ and CO. TROPOMI provides nearly global coverage each day at a spatial resolution which in August 2018 was 3.5 km×7 km (7 km×7 km in the SWIR). The equator crossing time is 13:30 LT (ascending node). Similar to OMI, TROPOMI is a nadir-viewing imaging spectrograph, employing a two-dimensional CCD, one dimension collecting the spectral information, the other being used for the spatial information. The TROPOMI instrument on board the S5P satellite provides data since November 2017 (Veefkind et al., 2012).

2.3 CHO.CHO retrieval from TROPOMI measurements

In recent years, several improvements on the retrieval of CHO.CHO have been reported. In 2014, Chan Miller et al. (2014) and Alvarado et al. (2014) presented new CHO.CHO retrieval algorithms applied to OMI measurements. These studies, similar to previous studies on GOME–2A data, introduced approaches to reduce interference by other absorbers, such as liquid water and nitrogen dioxide (NO$_2$). In this study, an optimized retrieval algorithm for CHO.CHO was developed,
building on the heritage from the OMI CHO.CHO retrieval presented by Alvarado et al. (2014), extended and applied to S5P measurements. Previous studies have shown that cross-correlations between references cross-sections, as well as instrumental structures and shifts in the wavelength calibration can introduce systematic errors in the retrieval. As a result, a strong dependence on the fitting window was identified in the retrieved CHO.CHO slant column densities, SCDs (Chan Miller et al., 2014; Alvarado et al., 2014). In this study, a fitting window from 433 to 465 nm was chosen, which is slightly larger than windows used in previous investigations (Vrekoussis et al., 2010; Alvarado et al., 2014). This fitting window, which enables the liquid water absorption to be retrieved, leads to a reduction in the number of negative CHO.CHO SCDs over oceanic regions in comparison to a shorter fitting window (e.g. 434–458 nm), as well as a reduction in the residuals. The wavelength range selected covers the strong absorption bands of CHO.CHO (452-457 nm), which have already been used in the past to retrieve CHO.CHO from ground and ship-based DOAS configurations as well as from satellites (Sinreich et al., 2007, 2010; Wittrock et al., 2006; Vrekoussis et al., 2009, 2010; Lerot et al., 2010; Chan Miller et al., 2014; Alvarado et al., 2014). In order to optimize the quality of the retrievals, a row-dependent daily mean Pacific spectrum from the region 50°S, 160°E – 50°N, 135°W is used as a background spectrum (Alvarado, 2016), which is computed by averaging over the whole latitude range (50°S – 50°N) for each across-track viewing direction independently. In addition, the mean CHO.CHO SCD over the region 30°S, 150°W – 30°N, 150°E is computed each day and subtracted from all SCDs to correct for possible offsets. A summary of the selected absorption cross-sections, and other parameters used in the retrieval, as well as a list of the species included in the retrieval, is shown in Table 1.

SCDs depend on observation geometry. VCDs are derived from the SCDs by use of so-called air mass factors (AMFs), which depend on the trace gas profile, surface albedo, aerosols, clouds, and on solar zenith angle and measurement geometry. As the focus of this study is the observation of CHO.CHO in biomass burning emissions, a simple CHO.CHO profile with a Gaussian distribution having its maximum peak at the altitude of the aerosol layer is used (see Figure 1-A). This is based on the assumption that CHO.CHO is found at the same location as the main plume of aerosol and other trace gases. The altitude of the aerosol layer was estimated from profiles retrieved by the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) (Vaughan et al., 2004) (Figure 1-B). These aerosol extinction coefficients (k_{ext}) profiles retrieved at 532 nm are also used in the calculation of the AMFs by the radiative transfer model SCIATRAN (Rozanov et al., 2013). The computations have been performed on a daily basis, assuming a single scattering albedo of 0.92 and a homogenous distribution of aerosols characterized by the mean profile in the whole region of study. The latter is computed from the average of all aerosol profiles taken over the region after removing cloud-contaminated pixels (see Figure 1-C). Clouds are not explicitly accounted for in the CHO.CHO and HCHO retrievals but data are filtered for the presence of clouds using an intensity criterion corresponding to a cloud radiance fraction of about 50%.
Table 1. Summary of retrieval parameters of CHO.CHO and HCHO from S5P with the respective absorption cross-sections used.

| Parameters                     | Formaldehyde (HCHO) | Glyoxal (CHO.CHO) |
|--------------------------------|---------------------|-------------------|
| Fitting window                 | 323.5-361 nm        | 433-465 nm        |
| Polynomial                     | 5 coefficients      | 5 coefficients    |

Cross-sections used:

| Cross-sections used                                | Formaldehyde (HCHO) | Glyoxal (CHO.CHO) |
|----------------------------------------------------|---------------------|-------------------|
| HCHO (Meller and Mootgat, 2000)                    | Yes (298 K)         | No                |
| CHO.CHO (Volkamer et al., 2005)                    | No                  | Yes (296 K)       |
| NO₂ (Vandaele et al., 1998)                        | Yes (220 K)         | Yes (220 K, 2294 K) |
| O₃ (Thalman et al., 2013)                          | Yes (293 K)         | Yes (293 K)       |
| O₃ (Serduchenko et al., 2014)                      | Yes (223 K, 243 K)  | Yes (223 K)       |
| BrO (Fleischmann et al., 2004)                     | Yes (223 K)         | No                |
| H₂O (Rothman et al., 2013)                         | No                  | Yes (296 K)       |
| Liquid water (Mason et al., 2016)                  | No                  | Yes (280 K)       |

Ring effect: Ring cross section calculated by SCIATRAN model (Vountas et al., 1998)

Non-linear ozone absorption effects, 2 pseudo absorption cross-sections (O₃ * \( \lambda \) + (O₃)²) from Taylor expansion (Puķīte et al., 2010)

Iterative spike removal (Richter et al., 2011) Applied

Intensity offset correction Linear offset (I/I₀)

Background spectrum Pacific region (50° N, 135° W – 50° S, 160°)
Figure 1. A) CHO.CHO and HCHO profiles assumed in the computation of AMFs. B) CALIPSO profile of aerosol extinction coefficients ($k_{\text{ext}}$), averaged over for all latitudes and longitudes of Figure 1-C, excluding cloudy scenes. C) Top panel: Example of CALIPSO Aerosol profile extinction coefficients retrieved at a wavelength of 532 nm. Aerosol and cloud optical depth are shown as a function of latitude and longitude for every single profile. Bottom panel: Colour coded $k_{\text{ext}}$ for every latitude and longitude in the selected region. Purple spots represent cloudy scenes. The black line depicts the aerosol layer height.

2.4 HCHO retrieval from TROPOMI measurements

The accuracy of DOAS retrievals of HCHO is limited by cross-correlations with strong absorbers in the UV (e.g. O$_3$) and the signal to noise ratio of the radiance spectra measured by the instrument. Here, an updated and optimized version of the formaldehyde retrieval developed by Wittrock et al. (2006) and Vrekoussis et al. (2010) is used, which applies a slightly larger fitting window extending from 323.5 nm to 361 nm, resulting in a reduction in the noise of the retrieved slant column densities. At wavelengths shorter than 336 nm, interference with O$_3$ is observed due to the small optical depth of HCHO, which is about three orders of magnitude smaller. This effect is compensated by applying the method described by Pukite et al. (2010), which consists of adding two additional pseudo-cross-sections to the fit ($\lambda\sigma_{O3}$ and $\sigma_{O3}^2$) (Pukite et al., 2010; De Smedt et al., 2008, 2015, 2018). The cross-sections of interfering species are included in the fit as listed in Table 1. In a manner similar to the retrieval of CHO.CHO, a synthetic ring spectrum (Vountas et al., 1998) is used to account for the Ring effect and a row-dependent daily mean Pacific spectrum from the region 50°S, 135°W – 50°N, 160°E is used as background spectrum. A latitude dependent offset correction based on SCDs from longitudes between 180° E and 160° E is applied to the data. As for CHO.CHO, VCDs are computed using AMFs, assuming a Gaussian shape for the distribution of HCHO at the layer where the aerosols are located in the plume. Figures 2-A and 2-B show examples of CHO.CHO and HCHO fit results for 10 August 2018, compared to the differential reference cross-section for a single measurement. For an individual CHO.CHO measurement, the detection limit is of the order of $5 \times 10^{14}$ molec.cm$^{-2}$, which is about 10 times smaller than the columns detected from emissions of the wildfires over the British Columbia region of Canada. For HCHO, the detection
limit is an order of magnitude higher \( (4.5 \times 10^{15} \text{ molec.cm}^{-2}) \). The detection limit of a single S5P measurement in this study has been estimated in a manner similar to that explained in Alvarado et al. (2004).

![Graph of CHO.CHO and HCHO](image)

**Figure 2.** A) Example fit for CHO.CHO from a single measurement of S5P taken at latitude 53.0° and longitude 125.6°W, on 10 August 2018 and for a solar zenith angle of 39.3°. B) Example fit for HCHO from a single measurement of S5P taken at latitude 59.1° and longitude 109.0° W, on 10 August 2018 and for a solar zenith angle of 44.6°. The black line depicts the scaled differential cross-section and the red line the fit. The SCD values for this example are \( 9.3 \times 10^{15} \) molec.cm\(^{-2}\) for CHO.CHO and \( 4.6 \times 10^{16} \) molec.cm\(^{-2}\) for HCHO, respectively. The detection limit for a single measurement from S5P is estimated to be \( 5.0 \times 10^{14} \) molec.cm\(^{-2}\) and \( 4.5 \times 10^{15} \) molec.cm\(^{-2}\) for CHO.CHO and HCHO, respectively.

### 2.5 Simulation of tracer transport with FLEXPART

In order to simulate the transport of emissions from the Canadian wildfires, forward simulations with version 10.3 of the FLEXible PARTicle dispersion model FLEXPART (Stohl et al., 2005; Pisso et al., 2019) have been performed. The model was driven by using hourly wind fields from the ECMWF ERA5 reanalysis (C3S) at 0.25° horizontal resolution. As a transport model, FLEXPART does not simulate the complete set of chemical transformations leading to the observed lifetimes of trace gases in the biomass burning plumes. However, performing simulations for tracers having different mean lifetimes yields a valuable piece of information in order to understand the observed plume evolution. An effective mean lifetime can be estimated by comparing the observed behaviour of the CHO.CHO and HCHO with FLEXPART simulations of different assumed tracer lifetimes.
In FLEXPART, the effective mean lifetime $\tau$ of an emitted tracer is treated as exponential decay with a given half-life ($t_{0.5}$); $\tau$ can then be calculated according to $\tau = t_{0.5}/\ln(2)$. As part of this study, FLEXPART simulations were carried out with half-lives of 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 hours, corresponding to effective mean lifetimes of $\sim2.9$, 5.8, 8.7, 11.5, 14.4, 17.3, 20.2, 23.1, 26.0, and 28.9 hours, respectively. As emission rates from wildfires are highly uncertain, the emission fluxes from the Canadian wildfires are assumed to be proportional to fire radiative power (FRP, see below for more details).

The emissions, prescribed in the model, are taken from the Global Fire Assimilation System (GFAS) daily FRP and plume height data (Rémy et al., 2017). Simulations were performed on a daily basis for the period 6 to 23 August 2018. For each day, all fires from the GFAS data, which had an FRP of more than 3 W cm$^{-2}$ were gridded to a 0.350° horizontal pattern. The model was then run forward in time for 120 hours, releasing the tracer for the first 24 hours (the full UTC day) from each of the 0.350° grid cells, assuming no temporal variation throughout the day. Vertically, the emissions within the grid cells were evenly distributed over the range of mean altitude of maximum injection heights given by the GFAS data for the respective grid cell. The output of the simulation contains gridded mass concentrations for each time step. Here, a grid with a horizontal resolution of 0.03125° was chosen, to match the resolution of the gridded satellite observations. Hourly output from the simulation was recorded and then vertically integrated to yield simulated tracer columns. In a post-processing step, for one specific mean lifetime, all simulation results (i.e., simulations for all fires on all days) were aggregated into one dataset. While the absolute tracer column density from the model output cannot be simply compared to the measurements, a comparison of the plume patterns and relative distribution between satellite observation and model output gives an indication about the meaningfulness of the prescribed mean lifetime. At this point, the aggregated model output for one effective mean lifetime consists of hourly latitude-longitude grids of vertical tracer columns throughout the whole study period. For comparison to the satellite observations, the hourly time slice closest to the time of overpass at 53°N was chosen.

3 Results and discussion

During August 2018, a high-temperature anomaly led to the outbreak of many fires in the Canadian Western province of British Columbia, resulting in the emission of large quantities of particles and traces gases that in turn affected air quality in the region. As shown in Figure 3-A and -B, the monthly average of CHO.CHO and HCHO vertical columns from S5P show strongly enhanced values over the fire region, suggesting that these fires were a large direct and/or indirect source of CHO.CHO and HCHO. Surprisingly, the CHO.CHO and HCHO enhancements are not limited to the main fire region but extend over large parts of Canada, where only a few fires were observed. In order to investigate the sources of CHO.CHO and HCHO and their distributions, 24-hour assimilation data of fire radiative power from the Global Fire Assimilation System (Kaiser et al., 2012) are analysed. Briefly, FRP is a measure of outgoing radiant heat from fires, measured in units of W cm$^{-2}$ and retrieved from space by the MODerate resolution Imaging Spectroradiometers (MODIS) on board of Terra and Aqua satellites (Justice et al., 2002). The assimilated FRP spatially aggregates all valid fire and non-fire observations from
both MODIS instruments onto a horizontal resolution of 0.1° x 0.1° and computes the total FRP sums for each grid bin (Justice et al., 2002). The FRP is also used as input in the FLEXPART simulation as described in section 2.5 as a proxy for emission strength. Figure 3-C shows a monthly average FRP map over North America for August 2018.

![Figure 3](image)

Figure 3. Monthly average of CHO.CHO (panel A) and HCHO (panel B) VCDs retrieved from the TROPOMI instrument on S5P for August 2018, and over North America (A and B). Panel C shows the integrated FRP from MODIS for the same period. The highest CHO.CHO VCD values are found over the locations of the most intense fires, as intuitively expected. The HCHO distribution over the fire regions is similar to that of CHO.CHO, but with some differences in the relative distribution. In addition, enhanced CHO.CHO and HCHO columns are also apparent over the south-eastern US, where large isoprene emissions occur. CHO.CHO and HCHO are also detected in plumes crossing central and eastern Canada, where no fires are identified in the FRP map. This pattern is best explained by the transport of CHO.CHO and HCHO emanating from the wildfires. However, CHO.CHO and HCHO have been reported to have short atmospheric lifetimes of about ∼2.2 and ∼4.0 hours during daytime, respectively (Atkinson, 2000; Volkamer et al., 2005a). Assuming that the lifetime in the plume is similar to that observed at the ground, we expect that CHO.CHO would be removed reasonably close to the fire sources. HCHO would be transported further but we would also expect that it would be transported no more than approximately twice as far as CHO.CHO.

Earlier studies by Wittrock et al. (2006) and Vrekoussis et al. (2009, 2010) showed that CHO.CHO is also observed over oceanic regions, where no CHO.CHO source is expected. The potential of a) a long-range transport of CHO.CHO and/or of CHO.CHO precursors from continental areas, and b) having an unknown oceanic CHO.CHO source were discussed as a possible explanation in part of these observations, but no firm conclusions could be drawn so far. In the present study, with the support of the simulations using FLEXPART, evidence of long-range transport of CHO.CHO and HCHO or its
precursors from biomass burning emissions is investigated. In this context the transport of CHO.CHO and HCHO during two fire plume episodes form different periods (07-10 and 20-21 August 2018) are discussed below.

3.1 CHO.CHO and HCHO emissions from the British Columbia wildfires: 07-10 and 20-21 August 2018

Figure 4-A shows daily maps of CHO.CHO and HCHO VCDs over Canada for the period 7 to 10 August 2018. The most intense wildfires are found on 7 August 2018 and remain detectable until 10 August 2018. Both CHO.CHO and HCHO plumes are detected on the first day of the fire. The CHO.CHO and HCHO distributions then change from day to day. However, a large plume is clearly visible on 10 August 2018. Enhanced CHO.CHO and HCHO columns are found at a distance of up to ∼1500 km from the fires, indicating transport over long distances.

To investigate possible transport pathways, forward simulations of the atmospheric transport with FLEXPART were calculated for the period when CHO.CHO and HCHO plumes are observed (see Figure 4-B), assuming an effective lifetime of 14.4 hours. The latter is significantly longer than lifetimes of CHO.CHO and HCHO found in the literature. On the other hand, the simulated pattern of air masses follows the same distinctive path as CHO.CHO and HCHO VCDs. The tracer simulated with FLEXPART spreads over the same area as CHO.CHO, providing evidence for the transport of CHO.CHO and HCHO and their precursors over continental Canada. This is more evident for the second period of interest in this study, which extends from the 20 to 21 of August 2018 (see Figure 7). While the spatial match of plume and model is good in this example, it is clear from the figure that an effective lifetime of 14.4 hours does not describe fully the extent of CHO.CHO and HCHO transported. Using shorter effective lifetimes for CHO.CHO and HCHO, taken from the literature would not reproduce the observations. However both lifetimes depend on conditions in the plume: on the diurnal photolysis and OH diurnal cycles as well as on wet/dry deposition processes and other oxidants. Consequently, comparisons of FLEXPART simulations with different effective lifetimes were performed for two selected days, as is shown in Section 3.2.
Figure 4. A) and B) Daily CHO.CHO and HCHO VCDs retrieved from S5P measurements for the period 7 to 10 August 2018. C) Distribution of a tracer with a lifetime of 14.4 hours simulated with FLEXPART for the same period. The CHO.CHO in the plume decreases on average from $3 \times 10^{15}$ molec.cm$^{-2}$ to $3 \times 10^{14}$ molec.cm$^{-2}$, while the HCHO has a different variation in the plume but at the end of the plume, it decreases from $3 \times 10^{16}$ molec.cm$^{-2}$ to $1 \times 10^{16}$ molec.cm$^{-2}$. The FLEXPART tracer column decreases from $3 \times 10^{6}$ to $0.3 \times 10^{6}$ for this specific effective lifetime of 14.4 hours.

3.2 Effective lifetimes of CHO.CHO and HCHO in the plume

Figure 5 shows the results of FLEXPART simulations assuming effective lifetimes for a surrogate chemical species of $\sim 2.9$, 14.4, 23.1, and 28.9 hours for 10 and 20 August 2018. From this figure, it is clear that only for the simulations having effective lifetimes of 23.1 hours or more, a significant fraction of the tracer emitted is present at the end of the plume as observed in the measurements. This is also illustrated in Figure 6, depicting CHO.CHO and HCHO maps for 10 August 2018. On top of these maps, contour lines are shown for the simulated air masses assuming effective lifetimes of $\sim 2.9$, 14.4, and 28.9 hours. It is evident that in both cases the tracer distributions simulated with longer effective lifetimes better describe the observed distribution of CHO.CHO and HCHO.

Figures 7-A, -B, -C present a second comparison of daily maps of CHO.CHO and HCHO VCDs with a FLEXPART tracer having an effective lifetime of 28.9 hours for 20 and 21 August 2018. It is evident that again, the tracer follows the distribution of CHO.CHO and HCHO observations, similar to the first period studied (see Figure 4). However, on 20 and 21 August 2018, the CHO.CHO and HCHO plumes spread over the ocean, where no sources are expected, up to the point at which the plume disperses after being transported over a distance of about $\sim 600$ km from the fires.
Figure 5. Daily maps of air masses simulated with FLEXPART for 10 and 20 August 2018 are shown (A and B) for selected effective lifetimes (≈2.9, 14.4, 23.1, 28.9 hours). C) Contour plots of simulations for the same lifetimes are compared for 10 and 20 August 2018.

The observed behaviour of the CHO.CHO and HCHO plumes is in contrast with the short atmospheric lifetimes resulting from their rapid removal by photolysis and reaction with OH. In addition, CHO.CHO oligomerises and thus is a source of SOA formation (Schweitzer et al., 1998; Jang et al., 2002; Liggio et al., 2005; Kroll et al., 2005; Loeffler et al., 2006; Volkamer et al., 2007; Fu et al., 2007; Myriokefalitakis et al., 2008; Stavrakou et al., 2009b, c). The simplest explanation of the observations of CHO.CHO and HCHO is that, during the fire events, both species are transported and/or produced during
transport over long distances, resulting in an effective lifetime of about 28.9 hours. This would imply the transport of VOC precursors of CHO.CHO and HCHO.

Figure 6. Daily maps CHO.CHO and HCHO VCD retrieved from S5P for 10 August 2018 compared with FLEXPART tracer simulations having three different lifetimes (∼2.9, 14.4, and 28.9 hours).

One reason for the longer range transport of the CHO.CHO and HCHO plumes is the injection of the biomass burning emissions into the free troposphere, where high wind speeds favour transport over long distances. This is a well-known effect that has also been observed for NO$_2$ in GOME-2 data (Zien et al., 2014). However, even at high wind speeds, the short lifetime of these species would result in much smaller dispersed plumes than the ones observed. There are three possible explanations for this apparent contradiction:

Reason 1: The lifetimes of CHO.CHO and HCHO could be significantly longer than expected in these biomass burning plumes if the OH mixing ratio and UV and visible radiation within the plume are much lower than outside the plume. There is, however, no indication that this should be the case; on the contrary, OH levels in the biomass burning plume are expected to be enhanced (Folkins et al., 1997), leading to a reduction of the expected CHO.CHO and HCHO lifetimes. In this context, it is interesting to investigate the NO$_2$ VCD observed. The NO$_2$ plumes coming from the biomass burning are shown in figure 8-B. During daytime NO$_2$ is removed in the gas phase by reaction with OH. Provided sufficient O$_3$ is present the photolysis of NO$_2$ produces NO and O which react respectively with O$_3$ to make NO$_2$ and oxygen molecules to make O$_3$. This is known as a “do nothing cycle”. NO$_2$ appears to decay relatively rapidly in the plumes coming from the fires. Our assumption that oxidation and photolysis of CHO.CHO and HCHO is relatively rapid, is thus not contradicted by the NO$_2$ decay in the fire plumes.

Reason 2: There could be an efficient recycling process between the gas and aerosol phase, resulting in the observed extended effective lifetimes of CHO.CHO and HCHO. However, this reason is considered unlikely, because there is not yet
any strong evidence of HCHO being a precursor of SOA formation, and as the shape of the plumes for both trace gases is similar, a similar mechanism is expected for both. Also, evidence for the release of CHO.CHO following the formation of oligomers in the aerosol phase, is limited (Kroll et al., 2005, and references therein).

Figure 7. A) and B) Daily CHO.CHO and HCHO VCDs retrieved from S5P measurements for the period from 20 to 21 August 2018. C) Tracer distribution simulated with FLEXPART for the same period assuming a lifetime of 28.9 hours. Enhanced CHO.CHO columns spread over the ocean in a pattern similar to that simulated by the model tracer.

Reason 3: The plume could contain CHO.CHO and HCHO precursors, i.e. VOCs, which are slowly oxidized, releasing CHO.CHO and HCHO along the trajectory. If true, this would result in an apparent increase in lifetime. In order to better assess the CHO.CHO and HCHO spatial distribution seen on 10 August 2018, two additional TROPOMI retrievals have been taken into account; the column-averaged dry air mole fractions of CO, retrieved by the algorithm described in Schneising et al. (2019), and the NO₂ VCD retrieved using an algorithm similar to the one described for the GOME-2 instrument (Richter et al., 2011) and using AMF calculated following the same approach as the one described before for CHO.CHO and HCHO (see section 2.3). The CO plume shows a similar spatial pattern to those of CHO.CHO and HCHO (see Figure 8-E). As CO is a relatively long-lived tracer of fire emissions, having a lifetime with respect to OH of months, this supports the fire origin of the plume. As noted above, NO₂ is removed by OH faster than CHO.CHO and HCHO. The NO₂ VCD enhancements, in contrast to those of CHO.CHO and HCHO, are limited to the proximity of the fire hot spots (see Figure 8-D). This behaviour agrees with that assumed for a molecule with a short atmospheric lifetime. A true-colour image from the Visible Infrared Imaging Radiometer Suite (VIIRS) clearly shows the distribution of smoke and aerosols produced because of the emission from the fires being transported and transformed (Figure 8-F). The distribution of the aerosol
appears qualitatively to be similar to the CHO.CHO, HCHO, and CO distributions. We infer that the transported plumes are mixtures of CO, CHO.CHO, HCHO, aerosol and presumably other pollutants released by the fire. It is interesting to note that CHO.CHO and CO follow mainly the main plume, while the HCHO distribution is more diffuse and shows enhanced values also over regions where a thinner aerosol plume is visible in the VIIRS image. This may possibly originate from other unidentified fires or another unknown source, which is not included in our FLEXPART simulations.

As additional information, the ratio of CHO.CHO-to-HCHO, $R_{GF}$, is presented in Figure 8-C. Larger values of $R_{GF}$ are found close to the location of the wildfires as already reported in previous publications (Vrekoussis et al., 2010). This is an indication of enhanced primary emissions of CHO.CHO relative to those of HCHO from fires. Lower $R_{GF}$ values are found closer to the end of the plume implying a decreasing production of CHO.CHO relative to that of HCHO during the transport of polluted air in the plume. Another potential explanation would be the mixing in of air from different origins, having lower CHO.CHO and/or higher HCHO concentrations, during the plume transport. This is however not confirmed by the observed CO behaviour, which shows a similar spatial distribution to CHO.CHO and HCHO.

The comparison of retrieved S5P columns and FLEXPART tracer simulations discussed is based on a number of simplifications. The observational conditions of the biomass burning plumes are complex, and aerosol scattering and absorption impact on the sensitivity of the retrievals. While this is taken into account by using air mass factors for elevated plumes positioned at altitudes derived from CALIPSO observations, there remains considerable uncertainty with respect to absolute values. Aerosol loading and optical properties will vary along the plume and thus will the retrieval sensitivities. This not modelled explicitly in this study. However, the differences apparent between the spatial distributions of CHO.CHO and NO$_2$, which are retrieved in similar spectral regions, provide evidence for the fact that measurement sensitivity does not explain the differences in the observed VCD plume patterns. Another crucial simplification is the assumption of a constant fire emissions and the proportionality of FRP and emission strength in the FLEXPART simulations. In reality, fire emissions will also depend on the type of biomass burned, the age of the fire, the time of the day and the environmental conditions, and this will have an effect on the trace gas distribution along the plume, which reflects both chemical transformation and the history of emissions. Modelling of this time-evolution is complex, if possible at all, and out of the scope of this study. However, the observation that both CHO.CHO and HCHO are present in the biomass burning plume after extended time periods and over long distances is robust and is best explained by the release of CHO.CHO and HCHO from the transformation of longer-lived precursors and/or efficient recycling processes in the plume as discussed above.
Figure 8. Panels A, B, D, and E show the CHO.CHO, HCHO, NO\textsubscript{2}, and CO columns, respectively retrieved from S5P measurements for 10 August 2018. Note that CO columns are unfiltered and only represent a qualitative description of the plume. The AMFs used for CHO.CHO, HCHO, and NO\textsubscript{2} are appropriate for the biomass burning plume only. Panel C depicts the calculated CHO.CHO-to-HCHO (R\textsubscript{GF}) for the same day. Panel F shows a true colour image of the aerosol distribution from VIIRS for 10 August 2018.

4 Summary and conclusions

The retrieval of CHO.CHO and HCHO VCDs from measurements of the TROPOMI instrument on board the Sentinel-5P satellite is reported. This will extend the datasets already available from the SCIAMACHY, GOME-2, and OMI instruments. The advantage of the high spatial resolution and low noise of TROPOMI for studying specific geophysical phenomena is well demonstrated in the features and plumes seen in the CHO.CHO, HCHO, CO, and NO\textsubscript{2} VCDs.

In this case study the satellite data show clear evidence for pyrogenic emissions of CHO.CHO and HCHO during the wildfire season in summer 2018 in British Columbia, Canada. The spatial and temporal pattern of the highest retrieved CHO.CHO and HCHO VCDs are associated with areas having high fire radiative power, as identified in the MODIS fire data products. This indicates that in these areas, pyrogenic emissions are the dominant source of CHO.CHO and HCHO.
addition to local enhancements of NO$_2$, CHO.CHO, and HCHO, close to the fires, extended plumes of elevated CHO.CHO and HCHO VCD are observed downwind from the fires. This is in contrast with the behaviour of NO$_2$, which is also transported but is short lived. The spatial and temporal CHO.CHO and HCHO distribution observed from satellite follows a similar pattern to that of CO, which is long lived, and that simulated by the FLEXPART dispersion model, initialized by tracer emissions starting at known fire locations. Enhanced CHO.CHO and HCHO were found in the S5P data up to 1500 km from their sources.

In order to obtain reasonable agreement between the model results and the measurements, an effective tracer lifetime of more than 20 hours and up to 28.9 hours needs to be assumed in the FLEXPART simulations. This is significantly longer than the anticipated lifetimes of CHO.CHO and HCHO. The transport of CHO.CHO and HCHO along the length of the plume could be associated with these trace gases being lifted from the boundary layer into the free troposphere, where high wind speeds lead to rapid transport. The long apparent lifetime of CHO.CHO and HCHO in the transported plumes could be explained by a real increase in their lifetime in the plume because of photochemical conditions in the plume, which we consider unexpected. Based on our current knowledge, the most probable explanation of the apparent long lifetime of CHO.CHO and HCHO would be formation within the plume caused by the oxidation of a mixture of longer-lived emitted VOC precursors (e.g. methanol, ethanol, acetylene, aromatics, glycolaldehyde, ethylene etc.), that form CHO.CHO and HCHO at different rates. Further research is needed to investigate how frequent such fire-related long-range transport events of VOCs are. The chemical mechanism of the formation of the CHO.CHO and HCHO in the plumes downwind of the fires needs to be identified. The assessment of the number of such fires events and their relevance for tropospheric O$_3$ and aerosol production downwind of the fires and air quality is required.

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