First global distributions of methanol and formic acid retrieved from the IASI/MetOp thermal infrared sounder

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Abstract

Methanol (CH$_3$OH) and formic acid (HCOOH) are among the most abundant volatile organic compounds present in the atmosphere. Their role in tropospheric chemistry stems from their influence on the oxidizing capacity of the atmosphere and, in the case of HCOOH, from its influence on the acidity of clouds and precipitation. In this work, we derive the first global distributions of these two organic species using the Infrared Atmospheric Sounding Interferometer (IASI) launched onboard the MetOp-A satellite in 2006. This paper describes the method used and provides a first critical analysis of the retrieved products. The retrieval process follows a two-step approach in which global distributions are first obtained on the basis of a simple radiance indexing (transformed into brightness temperatures), and then mapped onto column abundances using suitable conversion factors. For methanol, the factors were calculated using a complete retrieval approach in selected regions. In the case of formic acid, a different approach, which uses a set of forward simulations for representative atmospheres, has been used. In both cases, the main error sources are carefully determined: the average relative error on the column for both species is estimated to be about 50%, increasing to about 100% for the least favorable conditions. The distributions for the year 2009 are discussed in terms of seasonality and source identification. Global correlations between methanol and formic acid as well as correlations between these two species and carbon monoxide are also presented and discussed.

1 Introduction

Volatile Organic Compounds (VOCs) includes thousands of different carbon-containing gases present in our atmosphere at concentrations ranging from less than a pptv to more than a ppmv. Emitted from a large variety of processes (biogenic or anthropogenic) at the Earth’s surface, they have an important influence on the atmospheric composition and climate. VOCs are precursors to tropospheric ozone (Houweling et al.,
1998), they play an important role on the oxidizing capacity of the troposphere (Atkin-
son and Arey, 2003; Monks, 2005), they lead to the formation of secondary organic
aerosols (Tsigeridis and Kanakidou, 2007; Heald et al., 2008) and they impact on cli-
mate change in different indirect ways (Meinshausen et al., 2006; Feingold et al., 2003;
Charlson et al., 1987). In order to better understand and quantify their emissions and
the role they play in the Earth’s system, it is important to assess their atmospheric
distribution at the global scale.

1.1 Observation of VOCs from space

The first steps in measuring volatile organic compounds by infrared satellite sounders
were made during the last years, mostly using high-sensitive limb-viewing instruments.
A series of compounds, among which methanol and formic acid, have been observed in
young or aged biomass burning plumes with the ACE-FTS instrument (Rinsland et al.,
2004; Dufour et al., 2006; Coheur et al., 2007; Rinsland et al., 2007; Herbin et al.,
2009). Large datasets of that sounder, covering several years, have been gathered
to provide quasi-global distributions of these two species and to study their seasonal
variability (Rinsland et al., 2006; Dufour et al., 2007; Abad et al., 2009). Similarly
the observations of the MIPAS limb emission sounder have enabled mapping upper
tropospheric distributions of several organic species such as PAN, HCN and C$_2$H$_6$
(Glatthor et al., 2007, 2009); very recently global distributions of formic acid have also
been gathered and analyzed (Grutter et al., 2010). The possibility of probing these
VOCs lower in the atmosphere using nadir infrared sounders was suggested based on
local observations, both by TES (Beer et al., 2008) and IASI (Coheur et al., 2009), in
the latter case in large biomass burning plumes.

Other VOCs observations from space have been performed using ultraviolet (UV)
sounders. The GOME and OMI instruments provide measurements of formaldehyde
(Chance et al., 2000; Millet et al., 2008b), providing constrains on the emissions of iso-
prene (Shim et al., 2005; Palmer et al., 2006) and other non-methane volatile organic
compounds (NMVOCs) (Fu et al., 2007; Stavrakou et al., 2009). With the comple-
mentary use of SCIAMACHY (De Smedt et al., 2008) and with the GOME follow-on instrument onboard MetOp-A (GOME-2), a long-term dataset (14 years) of formaldehyde observations is now available. In addition, measurements of glyoxal have also been made from the SCIAMACHY instrument (Wittrock et al., 2006; Vrekoussis et al., 2009).

This study provides the first global distributions of methanol and formic acid observed by the IASI (Infrared Atmospheric Sounding Interferometer) instrument (Phulpin et al., 2007), briefly described in Sect. 2.1. This infrared nadir-looking sounder has already demonstrated its potential for the monitoring of different trace gases such as CO (George et al., 2009; Turquety et al., 2009), O₃ (Boynard et al., 2009), CH₄ (Razavi et al., 2009) and HNO₃ (Wespès et al., 2009). IASI has also demonstrated its high sensitivity to weak absorbers such as NH₃, for which global and local distributions have been obtained (Clarisse et al., 2009, 2010). The same method as the one used for retrieving global NH₃, and which relies on a simple difference of brightness temperatures, has been adapted to retrieve methanol and formic acid total columns. The method is described in Sect. 2.2 and a critical analysis of the resulting methanol field is provided in Sect. 3. The latter includes a first interpretation of the global distributions and seasonality of methanol as well as an error analysis. Section 4 provides similar analysis for formic acid. In addition, correlations between the two species and between them and CO are presented in Sect. 5.

Prior to this, a review of sources, sinks and previous measurements of methanol and formic acid is provided.

1.2 Methanol

Methanol (CH₃OH) is the most abundant organic species in the Earth’s atmosphere after methane and is also the main non-methane organic volatile compound in the mid to upper troposphere (Heikes et al., 2002). Because its main removal process is oxidation by OH (Atkinson, 1986), CH₃OH has a significant impact on the oxidizing capacity of the troposphere and on the global budget of tropospheric ozone (Tie et al., 2003).
Additional sinks include removal by dry and wet deposition and uptake by the ocean (Jacob et al., 2005; Millet et al., 2008a). Its mean lifetime is evaluated to be about 10 days in the free troposphere. The main emission sources of methanol are biogenic processes, involving plant growth (MacDonald and Fall, 1993; Nemecek-Marshall et al., 1995; Harley et al., 2007; Galbally and Kirstine, 2002) and plant decay to a lesser extent (Warneke et al., 1999). Other sources include biomass burning (Holzinger et al., 2005), oxidation of methane and other VOCs, as well as anthropogenic emissions from vehicles and industrial activities (Singh et al., 2000). There still exists large uncertainties in the relative source strengths, the atmospheric distribution and budget of CH$_3$OH (Singh et al., 2000; Tie et al., 2003; Jacob et al., 2005).

During the past few years, coordinated measurements campaigns have been conducted which provide, among other trace species, in situ and aircraft determination of methanol abundances, and from there information about its different emission sources. The diurnal and seasonal cycle of CH$_3$OH has been studied from in situ measurement in different types of environments such as forest (Karl et al., 2003, 2005), rural (Schade and Goldstein, 2006; Brunner et al., 2007; Jordan et al., 2009) or urban areas (Filella and Peñuelas, 2006; Nguyen et al., 2001) with a variety of techniques. The concentrations usually increase during daytime and exhibit also another strong increase just after sunset because of the boundary layer squeeze. Moreover, CH$_3$OH abundances are found to be higher during spring because of high plant growth emissions during that season. Methanol concentrations of about 4 ppbv have been reported in the amazonian region (Karl et al., 2007; Eerdekens et al., 2009). Aircraft measurements were also carried out over oceans (Singh et al., 2000, 2004) where background concentrations of a few hundreds of pptv were found. Airborne observations led also to the study of CH$_3$OH in several biomass burning plumes (Yokelson et al., 1999; Fischer et al., 2003; Yokelson et al., 2003; Holzinger et al., 2005) where volume mixing ratios (vmr) of up to several tens of ppbv were found. Observations of CH$_3$OH with ground-based infrared spectrometers were also recently conducted in Australia (Paton-Walsh et al., 2008) and in Arizona (Rinsland et al., 2009). The latter study provides an unprecedented 22 years
time series of free tropospheric CH$_3$OH; it does not report any significant trend over the years but shows a clear seasonality with a maximum in early July and a minimum during January.

The quasi-global distributions obtained from ACE-FTS (Dufour et al., 2007) have further revealed that the surface sources of methanol have a significant impact on its upper tropospheric concentrations, which are mostly driven by biogenic and biomass burning emissions in the Northern and Southern Hemisphere, respectively.

### 1.3 Formic acid

Formic acid (HCOOH) is one of the most abundant organic acid and has a strong influence on pH-dependent chemical reactions in clouds (Keene and Galloway, 1988). It has also been identified as a major sink for OH reactions in cloud water (Jacob, 1986). Although its sources and sinks are still poorly quantified, HCOOH is known to be emitted by various processes: biomass burning (Goode et al., 2000; Worden et al., 1997; Yokelson et al., 1997), biogenic emissions from vegetation (Keene and Galloway, 1984, 1988), emissions from soil (Sanhueza and Andreae, 1991), from ants (Graedel and Eisner, 1988), as a secondary product from organic precursors (Rasmussen and Khalil, 1988; Arlander et al., 1990) and also from motor vehicles (Kawamura et al., 1985; Grosjean, 1989). Formic acid can be also produced from the aqueous oxidation of formaldehyde in cloud and rain water (Chameides and Davis, 1983) as well as from the oxidation of formaldehyde by HO$_2$ radicals in the cold tropopause region (Hermans et al., 2005). It is mainly removed from the troposphere through wet and dry deposition but also through oxidation by the OH radical to a lesser extent. The resulting lifetime of HCOOH is estimated to be a few days in the boundary layer depending highly on precipitations (Sanhueza et al., 1996). The lifetime increases in the free troposphere, due to the very low OH-oxidation rate constant. HCOOH has been found to be a product of the isoprene oxidation by ozone (Jacob and Wofsy, 1988; Martin et al., 1991) and by OH radicals, in particular through the OH-oxidation of glycolaldehyde (Butkovskaya et al., 2006a) and hydroxyacetone (Butkovskaya et al., 2006b), which
are two important isoprene oxidation products, but also through the OH-oxidation of isoprene nitrates (Paulot et al., 2009).

In situ measurements of formic acid in the boundary layer have been carried out using different techniques in various parts of the world, from rural sites (Talbot et al., 1988; Puxbaum et al., 1988; Talbot et al., 1990; Hartmann et al., 1991; Helas et al., 1992) to urban areas (Grosjean, 1989; Khwaja, 1995; Granby et al., 1997; Souza et al., 1999). The observed HCOOH volume mixing ratio in the boundary layer ranges from 0.01 to 10 ppbv. Its diurnal cycle shows larger concentrations in the mid- to late afternoon (Martin et al., 1991; Hartmann et al., 1991) indicating larger sources during daytime (biogenic emission, photochemical reactions) and dry deposition at nighttime.

HCOOH measurements in the upper troposphere, performed during several aircraft campaigns (Reiner et al., 1999; Jaeglé et al., 2000; Singh et al., 2000), have reported mixing ratios from about 30 to 215 pptv. HCOOH has also been probed in different biomass burning plumes (Yokelson et al., 1999; Goode et al., 2000; Herndon et al., 2007) with concentrations of around ten ppbv; Worden et al. (1997) reported HCOOH total columns of 8.6 and $11.2 \times 10^{16}$ molec/cm² above two fire events in the USA using optical measurements in the infrared. Similar spectral measurements, which used the HCOOH ν₆ absorption band in the IR, were performed from a balloon (Goldman et al., 1984; Remedios et al., 2007), with mixing ratios up to 600 pptv at about 7 km height, or from the ground (Rinsland et al., 2004). The latter study gives insight on the seasonal variation of HCOOH, with a mean mixing ratio in the free troposphere from about 300 pptv in October–December to about 800 pptv in July–September, likely resulting from higher biogenic emissions during the growing season. Other ground-based measurements above Jungfraujoch were very recently analyzed over a 22 years period and show a similar seasonal cycle with a maximum occurring during summer as well as significant diurnal and day-to-day variability (Zander et al., 2010).

The first satellite observations in the upper troposphere were reported from the ACE-FTS instrument (Rinsland et al., 2006, 2007; Coheur et al., 2007) and were correlated to biomass burning events. Recent work performed with ACE-FTS on quasi-global ob-
observations of HCOOH reported an average mixing ratio of about 0.3 ppbv in the free troposphere with hot spots of up to 0.59 ppbv in tropical regions (Abad et al., 2009). Very recent global distributions were also assessed by the MIPAS sounder (Grutter et al., 2010) over a 6 years period. They report seasonal variations that may be associated to biogenic emissions with higher mixing ratios at 8 km during summer (about 100 pptv) than in winter (about 45 pptv). High concentrations were also observed in biomass burning plumes in the Southern Hemisphere. The nadir-viewing IASI sounder has also recently demonstrated the possibility to observe the HCOOH spectral signature in fire plumes (Coheur et al., 2009). In this study, we provide the first distributions of formic acid total columns above land, differentiated into four seasons for the year 2009. The retrieval method is slightly different from the one used for methanol because the conversion factor between brightness temperature differences and total columns is derived from a set of forward simulation. Details and error estimation are provided in Sect. 4.1.

It is important to note that a new set of HCOOH spectroscopic line parameters has been recently generated by Vander Auwera et al. (2007) and implemented in the latest versions of HITRAN and GEISA databases. The updated data set reports HCOOH line intensities larger by about a factor 2 compared to previous studies (Perrin and Vander Auwera, 2007). This implies that concentrations obtained from previous infrared retrievals were likely too high by the same factor.

2 Instrument and method

2.1 Description of IASI

The IASI instrument, launched onboard the MetOp-A platform in October 2006 on a polar sun-synchronous orbit, is a nadir-looking Fourier transform spectrometer that records the Earth’s outgoing radiation from 645 to 2760 cm\(^{-1}\) without gaps at an apodized resolution of 0.5 cm\(^{-1}\). Its field of view is a 2×2 matrix of circular pixels which
have a 12 km footprint diameter at nadir. IASI provides two global Earth coverages per day (about 1 280 000 spectra) thanks to the wide scans across its track (2200 km swaths). It offers also a very good signal-to-noise ratio, with a Noise Equivalent Delta Temperature (NEDT) at 280 K of about 0.2 K in the spectral region of interest (which extends from 975 to 1150 cm\(^{-1}\)). Moreover, with the successive launch of two other identical instruments, the IASI mission will provide consistent measurements over a 15 years period. A technical description of IASI and examples of applications for chemistry can be found in the review of Clerbaux et al. (2009). The IASI calibrated radiance spectra are disseminated in near-real time by the EumetCast system along with temperature, humidity profiles and cloud information (coverage, temperature and altitude). Only cloud free observations (when the cloud coverage for the pixel is below 2%) are taken into account for this study.

The measurement of methanol and formic acid concentrations from IASI is quite challenging due to their weak absorption and the interference of other molecules in the same spectral range (see Fig. 1). CH\(_3\)OH is observable using its C–O stretching absorption band located around 1033 cm\(^{-1}\). The spectral range also covers the \(\nu_6\) absorption band of HCOOH located near 1105 cm\(^{-1}\) and the \(\nu_3\) band of trans–HCOOH at 1777 cm\(^{-1}\) (Perrin et al., 2009), which can’t be detected in the IASI spectra because of strong water vapor interferences.

### 2.2 Retrieval approach

In order to take advantage of the very good spatial coverage of IASI we have chosen a simple, fast and robust approach based on brightness temperature differences (\(\Delta T_b\)), similar to the method already used for the retrieval of sulfur dioxide (Clarisse et al., 2008) and ammonia (Clarisse et al., 2009). It consists in two steps: (i) the determination of \(\Delta T_b\) globally and (ii) the conversion of \(\Delta T_b\) to total column amounts using one (global) or two (continental and oceanic) conversion factors.
The \( \Delta T_b \) corresponds to the difference between the brightness temperatures measured in one or several channels selected in the absorption signature of the target molecule \((T_{b,\text{target}})\) and the brightness temperature of nearby channels selected in a spectral region where the least absorptions are found \((T_{b,0})\). This is expressed in the following equation as

\[
\Delta T_b = \langle T_{b,0} \rangle - \langle T_{b,\text{target}} \rangle
\]

This quantity gives a handy estimate for the strength of absorption and hence of the concentration. However, the physics of the radiative transfer is not accounted for and the conversion of \( \Delta T_b \) to total columns requires a full radiative transfer treatment. For this purpose, we have retrieved \( \text{CH}_3\text{OH} \) total columns at various locations of the world with an inversion model based on the Optimal Estimation Method (OEM) (Rodgers, 2000) that includes a line-by-line radiative transfer model. This is implemented in the Atmosphit software developed at the Université Libre de Bruxelles (for more information see Clarisse et al. (2008) and Coheur et al. (2005)). The method is only applied in selected regions due to computational limitations. The conversion factor derived by matching the retrieved columns on the corresponding \( \Delta T_b \) is applied globally to derive the total column distributions.

For \( \text{HCOOH} \), we used an alternative conversion method only based on forward simulations (see Sect. 4.1).

In the next two sections we describe the different retrieval parameters (the chosen channels, spectral intervals and a priori information) and present the resulting global distributions for \( \text{CH}_3\text{OH} \) and \( \text{HCOOH} \), respectively.
3 Methanol retrieval and distributions

3.1 Retrieval settings

Methanol a priori profiles and covariance matrices were derived from distributions calculated by the IMAGESv2 global chemistry-transport model (Stavrakou et al., 2009). Two different vertical profiles were selected: an average continental and an average oceanic profile. This choice is justified by the existence of strong emission over continents resulting in enhanced concentrations in the boundary layer. These two profiles are illustrated on Fig. 2 together with their associated covariance matrix. The continental a priori profile has a surface mixing ratio of about 2.5 ppbv, about four times larger than in the oceanic profile. Above 4 km, the two profiles are similar with only slightly higher concentrations for the continental profile. The covariance matrices both show higher variabilities in the lower (0 to 2 km) and upper (14 to 18 km) troposphere. Over continental surfaces, the variabilities are larger by about 25%. In both cases, the correlation length is large.

As can be seen from Fig. 1, the methanol spectral signature is fully overlapped by the much stronger ozone band at 10 µm. A large spectral range is therefore needed in order to properly account for this strong interference in the retrieval process. The spectral range extending from 981.25 to 1038 cm$^{-1}$ was selected after several tests. CH$_3$OH partial columns are retrieved in 4 km thick layers from the ground to 16 km. Partial columns of O$_3$ in 6 layers up to 42 km and the total columns of H$_2$O and NH$_3$ are simultaneously adjusted. The regions selected for the retrievals are located above Congo (0–35° S, 10–50° E), Chad (0–25° N, 0–30° E), Brazil (0–20° S, 35–60° W), India (5–40° S, 70–90° E) and the Atlantic ocean (30° S–25° N, 10–40° W). These regions were selected because of their high $\Delta T_b$ values. An example of inversion is presented on Fig. 4 (top panel) for a case where the CH$_3$OH signature is unambiguous. The RMS of the residue when CH$_3$OH is not included in the retrieval is significantly higher ($3.1 \times 10^{-6}$ W/m$^2$sr$^{-1}$) than when it is taken into account ($2.5 \times 10^{-6}$ W/m$^2$sr$^{-1}$, 21485
this value being very close to the theoretical noise). This specific retrieval leads to a methanol total column of $5.57 \times 10^{16}$ molec/cm$^2$. On the bottom panel of Fig. 4, representative total column averaging kernel differentiated for continental and oceanic retrievals are illustrated. They correspond to the mean averaging kernel for all retrievals performed in the selected regions. In both cases, the sensitivity is maximum in the mid to upper troposphere from about 5 to 11 km, but retrievals over land show much higher sensitivity near the ground, largely due to the higher thermal contrast (Clerbaux et al., 2009).

For the global $\Delta T_b$ calculation, the three target channels, all chosen in the Q branch of CH$_3$OH (at 1033.25, 1033.5 and 1033.75 cm$^{-1}$, see Fig. 1), are also contaminated by O$_3$. Therefore, the baseline channels were also chosen inside the O$_3$ absorption band (at 1019, 1019.5, 1036.25, 1038, 1047 and 1048.5 cm$^{-1}$, see Fig. 1) in a way that maximizes the sensitivity of $\Delta T_b$ to the CH$_3$OH amount. To deal with the remaining contribution of O$_3$, the relationship between $\Delta T_b$ and O$_3$ concentrations has been derived using a set of forward simulations. For different columns of O$_3$ (ranging from 185 to 407 DU), the spectrum and $\Delta T_b$ were calculated with a fixed amount of CH$_3$OH ($4 \times 10^{16}$ molec/cm$^2$). The results, presented on Fig. 4 assuming a typical midlatitude summer atmosphere (1976 US standard model), show a very well defined linear correlation between the total column of ozone and the calculated $\Delta T_b$. Similar results were obtained for other typical atmospheres and an average linear dependence was computed (with a slope of $9.02 \times 10^{-4}$ K/DU). The same type of simulations were performed to derive the influence of water vapor on the CH$_3$OH $\Delta T_b$ (gray curve in Fig. 4). From these relationships a corrected $\Delta T_b$ for methanol which minimizes the dependence on O$_3$ and H$_2$O is calculated as follows

$$\Delta T'_b = \Delta T_b + 9.02 \times 10^{-4} C_{O_3} + 8.13 \times 10^{-25} C_{H_2O}$$

(2)

where $C_{O_3}$ and $C_{H_2O}$ are the total columns of O$_3$ in Dobson unit and of H$_2$O expressed in molec/cm$^2$, respectively. This correction is applied to all observations using the total columns of O$_3$ and H$_2$O retrieved from IASI with a near-real time algorithm based on
The next step of the method, i.e. the determination of a suitable conversion factor between $\Delta T'_b$ and CH$_3$OH total columns, is performed based on the retrievals in selected regions of the world. Only retrievals results with a DOFS (Degrees Of Freedom for Signal, given by the trace of the averaging kernel matrix) higher than 0.75 and a RMS of the residual lower than $4 \times 10^{-6} \, \text{W/(m}^2 \text{sr m}^{-1})$ are taken into account. This translates to a total of 5147 and 2849 observations above land and oceans, respectively. The corresponding scatter plots are shown in Fig. 5. In both cases, a linear fit shows good correlation coefficient (about 0.75). The slope for the retrievals over land is found to be much larger than over oceans. Two different conversion factors are therefore used and applied to the $\Delta T'_b$ calculated globally:

$$C^{\text{land}}_{\text{CH}_3\text{OH}} = 4.482 \times \Delta T'_b$$

(3)

$$C^{\text{ocean}}_{\text{CH}_3\text{OH}} = 2.987 \times \Delta T'_b$$

(4)

where the CH$_3$OH total columns ($C_{\text{CH}_3\text{OH}}$) are expressed in $10^{16} \, \text{molec/cm}^2$. It is important to note that for the derivation of the global distributions, only cloud free measurements recorded during daytime were taken into account. This is justified because daytime measurements are generally characterized by a positive thermal contrast and are therefore more sensitive to the lower troposphere.

### 3.2 Global distributions

The method proposed above allows to derive the first global distributions of methanol. In order to shed light onto seasonal variations, the four seasons have been differentiated as follows: DJF (December 2008, January 2009 and February 2009), MAM (March, April and May), JJA (June, July and August) and SON (September, October and November). The resulting distributions averaged on a $0.5^\circ \times 0.5^\circ$ grid are shown in Fig. 6. Note that measurements above sand surfaces, which causes erroneous
high CH$_3$OH concentrations due to spectrally resolved surface emissivity (Wilber et al., 1999) have also been discarded.

Figure 6 shows large seasonal variations in the methanol columns. Higher concentrations are found in the northern hemisphere during spring and summer (up to $4 \times 10^{16}$ molec/cm$^2$ in Central and Northern Asia) when vegetation is growing. In the Southern hemisphere, the highest concentrations are found during the dry season (SON) and may be related to biomass burning. CH$_3$OH is also observed over oceans (with values around $2 \times 10^{16}$ molec/cm$^2$) mostly between Africa and South America but also in the whole Northern hemisphere in spring and summertime. The presence of CH$_3$OH in remote oceanic regions is probably largely due to transport of continental emissions although oceanic emissions (Millet et al., 2008a) and the ubiquitous methane oxidation might also contribute. Methanol total columns range from about $0.01 \times 10^{16}$ molec/cm$^2$ above sea surfaces to $5.40 \times 10^{16}$ molec/cm$^2$ over large emission regions.

During the Northern Hemispheric winter (DJF), methanol hot spots of low intensity are found in the Southern Hemisphere (South America, South Africa and Western Australia) above vegetated areas where CH$_3$OH emissions may be related to plant growth. When comparing the distribution with AATSR (Arino et al., 2005) fire count maps, we find a high degree of coincidence in Africa between 5 and 15$^\circ$ N, suggesting a possible biomass burning contribution. During springtime (MAM), this specific region is subject to enhanced CH$_3$OH columns which is possibly due to an increase in the fire numbers and intensities. Strong enhancements are also observed over India and to a lesser extent over Burma, Manchuria and Mexico, which can be at least partly related to biomass burning. In contrast, biomass burning is unlikely to be a dominant source in the Northern Hemisphere except in some regions (Kazakhstan, East Russia, Alaska) during JJA. It can be seen that CH$_3$OH concentrations are progressively increasing from winter (DJF) to summertime (JJA). This can be explained by the seasonal cycle of the vegetation source which presents a maximum in late spring (Schade and Goldstein, 2006; Rinsland et al., 2009). During fall (SON), CH$_3$OH concentrations decrease again.
in the Northern Hemisphere and increase in the Southern Hemisphere. Again, biomass burning is likely responsible for the strong enhancements in South America, Congo and Northern Australia.

Although biomass burning is assumed to be a weak emission source of methanol (accounting for about 5% of total emissions according to current inventories), the main hot spots in the global distributions appear to be possibly related to fires, indicating a possible underestimation of the biomass burning source in models. Caution is required, however, because pyrogenic methanol is usually transported higher in the troposphere where the IASI sensitivity is larger. This is consistent with the fact that biomass burning has been found to be a significant source of methanol in the upper troposphere (Dufour et al., 2007). The assimilation of IASI data into models should help determining the respective contributions of biogenic and fire emissions to the global methanol budget.

3.3 Error assessment

One of the disadvantages of the method described above is that it does not provide an estimation of the systematic errors associated with the retrieved total columns. Because we are deriving the CH$_3$OH columns from a weak signal, the associated error is expected to be quite large. An estimation of the error on the CH$_3$OH columns derived from IASI can be based on forward simulations. For this purpose, we used a large set of different atmospheres compiled in an ECMWF database (Chevallier, 2001). Different input profiles are used for CH$_3$OH, corresponding to the different continental profiles taken from the IMAGESv2 model. The total columns used as input for the simulations are then compared to those retrieved from the simulated spectra using the same method as described above. The difference between the two columns gives a fair estimate of the absolute column errors.

It turns out that this absolute difference increases when the amount of CH$_3$OH in the boundary layer (between the surface and 3 km height) increases. It follows that the high concentrations of methanol in the boundary layer (close to the emission sources) will not be well reproduced by the $\Delta T_b$ method. This is consistent with the averaging ker-
nel shape and the well known limited sensitivity of the infrared measurements toward low altitudes. Figure 7 shows the histogram of the relative difference between the total columns used as input in the forward simulations and the calculated ones. The distribution is similar to a normal distribution with a mean very close to zero (0.6%). The standard deviation (48.9%) provides our best estimate of the relative error on the retrieved methanol total column. This value is, however, clearly a lower bound for regions located close to emission sources and with low thermal contrast. In these regions, based on our analysis, errors as high as 100% are likely.

4 Formic acid retrieval and distributions

4.1 Retrieval settings and errors

In the case of formic acid, the target channel for brightness temperature has been chosen in the Q-branch at 1105.0 cm$^{-1}$ which is the strongest absorption feature detectable in the IASI spectrum. The reference channels were chosen on both sides at 1103.0 and 1109.0 cm$^{-1}$. The Δ$T_b$ values computed globally over one year range from about 0 to 5 K. As there exist large uncertainties on the vertical profile of formic acid, we have chosen here to rely on a composite vertical profile for the a priori. It was built from aircraft measurements for the low and free troposphere and from ACE-FTS for the upper troposphere. Also, because the lifetime of HCOOH is short and there is no known emissions from oceans, we have chosen to limit the analysis to continental profiles. The a priori profile is an average of profiles collected over the USA (25–55° N, 230–290° E) including (i) aircraft data from the INTEX-B C-130 campaign in April and May 2006 (Kleb et al., 2010) between 0–5 km, (ii) the arithmetic mean between INTEX-B data and ACE-FTS data (Abad et al., 2009) measured from March to May for altitudes between 6 and 8 km, (iii) and an averaged ACE-FTS profile between 9 and 11 km. The resulting profile, illustrated in Fig. 8, has a surface mixing ratio of about 750 pptv, which smoothly decreases as the altitude increases, down to less than 100 pptv above 7 km. Concentration above 11 km have been linearly extrapolated up to 20 km.
As in the case of methanol, conversion factors between the $\Delta T_b$ and the HCOOH total columns were tentatively derived based on OEM retrievals in selected regions around the world. Because of the weak signal and the presence of water vapor interferences, the retrievals are unstable and lead to large errors. Forward simulations using the ECMWF database and varying the HCOOH concentrations (scaling of the profile) were conducted (as for CH$_3$OH) to compute absolute errors as the difference between the true columns (input of the forward model) and those retrieved from the $\Delta T_b$. Figure 9 illustrates in gray the histogram of the relative errors. The mode of the errors is at about 60.0% suggesting a strong bias between the calculated and simulated total columns. Therefore, an alternative method has been used to derive the conversion factor between the $\Delta T_b$ and the total columns. Relying only on the forward calculations, it minimizes also the dependence upon the water vapor content ($C_{H_2O}$ expressed in molec/cm$^2$) and accounts for the varying sensitivity of the measurement to the local thermal contrast ($\tau$). The following equation is used

$$C_{\text{HCOOH}} = \frac{\Delta T_b - b_1 \tau - b_2 \tau C_{\text{H}_2\text{O}} - c_1 C_{\text{H}_2\text{O}} - c_2}{a_1 \tau + a_2 \tau C_{\text{H}_2\text{O}}}$$

(5)

with the parameters:

- $a_1 = 0.024$, $a_2 = 4 \times 10^{-26}$,
- $b_1 = 0.005$, $b_2 = 1 \times 10^{-26}$,
- $c_1 = 0.131 \times 10^{-23}$, $c_2 = 0.139$,

and where HCOOH total columns ($C_{\text{HCOOH}}$) are expressed in $10^{16}$ molec/cm$^2$. This mapping of $\Delta T_b$ onto total columns of HCOOH provides much better results. However, a significant dependency on the thermal contrast remains, with lower errors found for higher thermal contrast values. Although it may be a quite conservative criterion, we have chosen to consider only the cases for which the thermal contrast is higher than 5K. The resulting histogram of the relative errors between the simulated and calculated...
HCOOH total columns is shown in black on Fig. 9. It is similar to a normal distribution, with its mean being equal to −0.8%. Our estimation of the error on the formic acid total column is given by the standard deviation of the errors, which is about 60%. This error is only slightly higher than the error found for the CH₃OH columns, but only applies here to favorable situations with large thermal contrast.

4.2 Global distributions

The global distributions of formic acid for the four seasons are illustrated in Fig. 10, on a 0.5° × 0.5° averaged grid. Only cloud free observations recorded during daytime and with a thermal contrast higher or equal to 5K were taken into account. The latter constrain removes unfortunately many observations at high latitudes (no observations above about 45° N in winter and about 65° N during summer). Grid points which include less than ten HCOOH measurements were also filtered out. As for CH₃OH, clear seasonal variations are observed. The retrieved HCOOH total columns range from background values of less than 0.5 × 10¹⁶ molec/cm² above Europe and North America to 5 × 10¹⁶ molec/cm² above fire events, mainly during summer 2009 in Africa. These high formic acid total columns in fire plumes are in good agreement with the values reported by Coheur et al. (2009) and Worden et al. (1997) if we account for the factor 2 resulting from the use of the improved line parameters (Vander Auwera et al., 2007).

The 2009 northern hemispheric winter season (DJF) shows the lowest number of observations. During that period, enhancements of HCOOH which might be partly due to biomass burning are detected in the western-central region of Africa and to a lesser extent in South America. During spring (MAM), we observe a decrease in the HCOOH total columns above Africa and South America. High concentrations are also found in Asia (India, Burma and Manchuria) which are well correlated with CH₃OH hot spots. The peak of the biomass burning season in South America and Southern Africa happens usually around August–September whereas in Australia most of the burning occurs around October–November (Gloudemans et al., 2006). Together with the minimal washout of HCOOH occurring during the dry season, it probably largely
explains the high HCOOH total columns observed during JJA above Congo and Brazil as well as in Northern Australia during the SON period. Other regions of high HCOOH columns can be associated to boreal fires during the JJA period such as Eastern Russia and some regions of North America. Large HCOOH columns are also observed on the East coast of North America and in East China. They might partly be due to anthropogenic activities. Finally, the very widespread hot spots found during SON above Amazonia and Central Africa do not seem to be related to fires and very likely points to biogenic emissions of either HCOOH or HCOOH precursors. Several common patterns are found in the distributions of HCOOH and \( \text{CH}_3\text{OH} \) columns, probably due to their common emission sources (such as biomass burning and plant growth). Also note that the seasonality observed here is in good agreement with that reported from ACE-FTS (Abad et al., 2009) and from MIPAS (Grutter et al., 2010).

5 Correlations

In this section, we present a first analysis of the global correlations between methanol and formic acid as well as an example of global correlation of these two species with the IASI CO total columns (George et al., 2009) for the 2009 summer period (JJA) when biogenic emissions are largest in the Northern Hemisphere. The scatter distributions between \( \text{CH}_3\text{OH} \) and HCOOH total columns, shown in Fig. 11, are differentiated into four seasons in the same way as done before for their global distributions. For each season, methanol total columns are found to be generally higher than the formic acid columns. The DJF and SON periods show very similar linear relationships with good correlation coefficients (about 0.70), confirming the similarities between their emission sources observed in the global distributions. The correlations in spring (MAM) and summer (JJA) are slightly worse with coefficients of about 0.6 and 0.4, respectively. Their slopes are also found to be lower (about 0.4 for MAM and JJA against 0.75 for DJF and SON) indicating higher emission of \( \text{CH}_3\text{OH} \) than HCOOH from plant growth in the Northern Hemisphere. During JJA and SON, cases with relatively higher HCOOH
concentrations compared to CH$_3$OH are found, which are mostly located in the Southern Hemisphere, in regions affected by biomass burning.

Concerning the correlations with carbon monoxide, different studies have already demonstrated the relationship between VOCs and CO inside fire plumes (Yokelson et al., 1999; Goode et al., 2000; Coheur et al., 2009). Figure 12 shows the relationship of CO with CH$_3$OH (top panel) and HCOOH (bottom panel) for all observations above land surfaces during JJA. The colors discriminate between different latitudinal bands of 20° width. The black line represents the correlation between the two species in biomass burning plumes (inferred over selected fire regions identified with the AATSR fire data and mostly located above Africa, between 25°S and 10° N). In this way, observations influenced by biomass burning can clearly be identified on each plot and are found to be mostly located in the tropical belt. Methanol and formic acid north of 40° N (orange and red) are higher than the biomass burning line. This suggests that at these latitudes, HCOOH and CH$_3$OH are mostly emitted by biogenic processes. When comparing HCOOH with CO, most points located at mid northern latitude (between 20° N and 40° N, in yellow) present a much lower ratio than for biomass burning. For CH$_3$OH, these points are however well correlated to biomass burning. Further work is needed to assess the usefulness of the ratios between these VOCs and CO to discriminate specific emission processes.

6 Conclusions and perspectives

In this study, we have retrieved methanol and formic acid from the data provided by the IASI sounder. Using a radiance indexing method and the calculation of brightness temperature differences, first global distributions are computed. They are provided as total columns, after careful conversion of the brightness temperature differences. The conversion has been achieved based on a set of retrievals in selected regions for methanol and on forward simulations for formic acid. Taking full advantage of the IASI spatial and temporal coverage, unprecedented information on the location and origin
of sources have been acquired. The simple retrieval method used here does not allow the determination of individual error for each observations. We have estimated, using a large set of representative forward calculation, global errors of about typically 50% and 60% for the methanol and formic acid total columns, respectively. Although these errors are significant, this robust method takes advantage of the very large number of IASI measurements at low computational cost. In this way, we provide global observations for these two volatile organic compounds.

The global distributions shown in this study highlight strong seasonal variations for methanol and formic acid with maximum total columns values evaluated at 5.4 and $5.0 \times 10^{16}$ molec/cm$^2$, respectively. The strong enhancements seen in the global maps can be largely attributed to biomass burning (mostly in tropical regions). The main seasonal patterns, especially at mid-latitudes where we find higher columns in spring and summer, can be explained by variations in biogenic emissions and increased plant growth. Anthropogenic emissions could not been clearly identified in these distributions.

Methanol and formic acid were shown to be fairly well correlated, with correlation coefficient ranging from 0.4 to 0.7 depending on the season. This highlights the potential similarities between their emission sources. For summer 2009, the correlations between the two species and carbon monoxide are also presented. It suggests interestingly that the use of VOCs/CO ratios could help to differentiate the emissions of CH$_3$OH and HCOOH from biomass burning and biogenic sources.

It is anticipated that the assimilation of these data in a global chemistry model will help to improve the determination of the emission fluxes for these two species.

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Fig. 1. Top panel IASI normalized radiance spectrum in the spectral region between 950 and 1200 cm$^{-1}$ containing methanol and formic acid absorption bands. Bottom panels Contribution to the IASI spectrum of different atmospheric species plotted in transmittance. The vertical lines indicate the target channels (in red) and the baseline channels (in blue) which are used for the $\Delta T_b$ determination (nine channels are used for CH$_3$OH, and three for HCOOH). See Sect. 2.2 for details.
Fig. 2.  *Top panel* Illustration of the two CH$_3$OH a priori profiles (continental and oceanic) derived from the IMAGESv2 CTM model for the year 2007.  *Bottom panel* Plot (expressed in %) of the associated covariance matrices (left: land, right: ocean) that illustrates the variability through the diagonal elements and the correlation between the different levels with off-diagonal values.
Fig. 3. **Top panel** Example of a methanol retrieval from an IASI spectrum recorded over Namibia (20.16°S–21.50°E) on October 20, 2008. The observed (blue curve) spectrum is shown together with the fit residue (in cyan). The dark green curve is the fit residue when CH$_3$OH is not taken into account in the retrieval, the red curve represents the calculated CH$_3$OH contribution to the spectrum and the dashed vertical line indicates the detectable CH$_3$OH absorption band. **Bottom panel** Mean total column averaging kernels presented for retrievals performed over land (green curve) and over ocean (blue curve).
Fig. 4. Illustration of the influence of water vapor and ozone concentrations on the methanol $\Delta T_b$. Simulations were performed for the midlatitude summer model with varying concentrations of $H_2O$ (black squares) and $O_3$ (red squares) while the $CH_3OH$ amount was fixed. In both cases, a linear dependence is found.
Fig. 5. Correlation between the retrieved total columns of methanol and the corresponding $\Delta T_b$ for various regions (corrected for $O_3$ and $H_2O$ dependency, see text for details). The conversion factors are given by the slopes of the linear fit (gray curve) separated for retrievals above land (Top panel) and above ocean (Bottom panel).
Fig. 6. Seasonal distributions of methanol total columns for the year 2009. The white areas correspond to a filter for sandy scenes where emissivity is uncertain.
Fig. 7. Histogram of the relative errors between the simulated CH$_3$OH total columns and the total columns derived from the $\Delta T_b$ calculation.
Fig. 8. HCOOH a priori profile derived from the combined aircraft and ACE measurements. See text for details.
**Fig. 9.** Histograms of the relative error between the simulated total columns of HCOOH and the HCOOH total columns obtained from brightness temperature differences. The gray histogram is derived from the conversion which uses OEM retrievals and the black one corresponds to the conversion obtained with simulated data. The latter, which is much less biased is used to obtain the global distributions (see Sect. 4.2).
**Fig. 10.** Seasonal distributions of formic acid total columns for the year 2009. Only cloud free observations recorded during daytime above continents along with a thermal contrast higher than 5 K were considered.
Fig. 11. Global correlations between methanol and formic acid total columns differentiated for each season of the year 2009. The resulting linear fit is represented in red. The one to one line is shown in gray.
Fig. 12. Continental correlations of CO with CH$_3$OH (Top panel) and with HCOOH (Bottom panel) presented for the 3 month period of summer 2009. The colors represent different latitudinal bands of 20° width and the black lines correspond to a correlation between the two species in regions where the biomass burning source is dominant (see text for more details).