

Ground-based FTIR measurements of volatile organic compounds: precious data for model and satellite validation

by Corinne Vigouroux, Belgian Institute for Space Aeronomy, Brussels, Belgium (corinnev@oma.be)

The global emission budget of many volatile organic compounds (VOCs), as needed in chemistry-transport models (CTM), is still very uncertain despite their great impact on Earth's environment and human health. Recently, satellite measurements of VOCs have been performed (Razavi et al., 2011; González Abad et al., 2009), improving the current knowledge of these species on a global scale. However, such new satellite data suffer from the sparsity of available data for their validation. Either balloon or aircraft campaigns are used which do not provide a good temporal nor spatial coverage, or in situ measurements which are useful for model validation but not adapted for the satellite data, that have usually a poor sensitivity at the ground. Network ground-based FTIR measurements provide long time-series and total column data of VOCs and are therefore very good candidates for supporting the evaluation of both satellite and model data. We summarize in this letter the previous exploitation of ground-based FTIR VOCs measurements, focusing on the ones that have been used for satellite and/or model data comparisons, demonstrating their usefulness.

Many ground-based FTIR studies have been dedicated to VOCs measurements: when long time-series are available, these observations improve our knowledge about the atmospheric concentrations and short-term, seasonal and inter-annual

variabilities of the VOCs. Considering their long lifetime, ethane (80 days) and acetylene (2 weeks) are well-known tracers for the transport of tropospheric pollution, and have already been measured by ground-based FTIR spectrometry at several NDACC stations in the Northern Hemisphere (Mahieu et al., 1997; Notholt et al., 1997; Rinsland et al., 1999, Zhao et al., 2002, Mahieu et al., 2008) and in the Southern Hemisphere (Rinsland et al., 2001, 2002; Paton-Walsh et al., 2010; Vigouroux et al., 2012). More recently, methanol and formic acid, shorter-lived species with global lifetimes of 6 days and 3-4 days, respectively, have also been measured, in the Northern Hemisphere (Rinsland et al., 2004, 2009; Zander et al., 2010), the Southern Hemisphere (Paton-Walsh et al., 2008, Vigouroux et al., 2012), or both (Paulot et al., 2011). FTIR measurements of formaldehyde (lifetime of few hours) were made by Notholt et al. (1997) and Mahieu et al. (1997), and more recently in the Southern Hemisphere by Vigouroux et al. (2009), Jones et al. (2009), and Paton-Walsh et al. (2010). An important source of VOCs in the Southern Hemisphere being the biomass burning emissions, in most of the above cited references, the authors evaluate the enhancement ratio of the VOCs species relative to CO, provided by the correlation between the species and the CO total columns. This ratio can then be compared to the pyrogenic emission factors used in the CTMs as input parameters.

Some of these ground-based measurements have been used for satellite validation. In the recent paper of Duflot et al. (2012), the HCN and C₂H₂ total columns from IASI are validated with FTIR data from Reunion Island (Vigouroux et al., 2012) and Jungfraujoch (Mahieu et al., 2008), showing that IASI captures well the seasonality of these species except in the case of HCN at Jungfraujoch. The formaldehyde measurements at Reunion Island were compared to the SCIAMACHY total columns in Vigouroux et al. (2009). This study shows a very good agreement,

especially in 2004, with a day-to-day variability well reproduced by both data sets. Both instruments show the same seasonal cycle with a minimum in local winter, due to the lower OH concentrations during this period. The formaldehyde measurements at Wollongong also compared well to GOME columns (Jones et al., 2009). Considering the large amount of available VOCs measurements from FTIR stations, and the success of these few studies for satellite validation, we believe that there is room for this kind of collaboration with the satellite community.

Comparisons between ground-based measurements and models are needed to evaluate the chemical and transport processes in the models and the input parameters (emission factors, fire and anthropogenic emission databases). In the papers by Vigouroux et al. (2009) and Jones et al. (2009), the formaldehyde time-series are compared to model simulations: in the former paper the CTM IMAGESv2 is used, while the latter uses a simple box model of methane oxidation by OH, which is the largest source of formaldehyde. Both comparisons show an underestimation by the models. Such comparisons help to question the CTM models, such as IMAGESv2. First, the OH concentrations can be underestimated in the model. Second, the fire injection heights and the convective updraft fluxes which are uncertain in IMAGESv2, could explain why the high day to day variability observed in the data are not reproduced by the model. Lastly, the pyrogenic and biogenic emissions at Madagascar could be underestimated. The underestimation of pyrogenic emissions, in the Global Fire Emission Database v2 (GFED2, van der Werf et al., 2006) used in the IMAGESv2, seems to be confirmed in Vigouroux et al. (2012), which concludes that also GFED3 (van der Werf et al., 2010) underestimates the pyrogenic emissions, especially in the late September-October period in south-eastern Africa - Madagascar region. Another interesting finding of the comparisons between model and FTIR data at Reunion Island concerns the budget

of methanol and acid formic. Indeed, the excellent correlation of CH_3OH and HCOOH with CO between August and November suggests that, despite the dominance of the biogenic source of these compounds on the global scale, biomass burning is their major source at Reunion Island during this period. This was expected for other species such as HCN, C_2H_6 and C_2H_2 , but less so for methanol and formic acid given the low contribution of fires to their global budget (2% and 14%, respectively). This conclusion demonstrates the need for models to use, in addition to satellite data, some independent ground-based measurements. Indeed, while satellite data are very useful for source inversion studies, as made in Stavrakou et al. (2011) for methanol and Stavrakou et al. (2012) for formic acid, in which IMAGESv2 emission budgets were constrained by IASI data, the comparisons with ground-based data can validate or temperate the inversion study. As an example, we show in Fig. 1, the FTIR and IMAGESv2 simulations of methanol and formic acid. The optimised IMAGESv2 simulations, using IASI data, are shown in green in Fig. 1. We observe that the CH_3OH IASI derived emissions remain too low during the fire season, suggesting that IASI may underestimate CH_3OH in this period in the Southeastern Africa-Madagascar region.

Formic acid (HCOOH) provides another good example of what can be learned from ground-based FTIR observations. It is well-known that the CTMs strongly underestimate formic acid observations: it is a hot topic today to find the missing source(s), and this has been the subject of two recent studies, that have used FTIR ground-based data from several stations: Paulot et al. (2011) in ACP, and Stavrakou et al. (2012) in Nature Geoscience. As already mentioned, the latter paper is based on source inversion using IASI data, and leads to an increase of the global source of HCOOH from 36 to 102 Tg yr⁻¹, obtained mainly by the introduction of a large source due to the photochemical degradation of biogenic NMVOCs. Although the IMAGESv2 optimization of

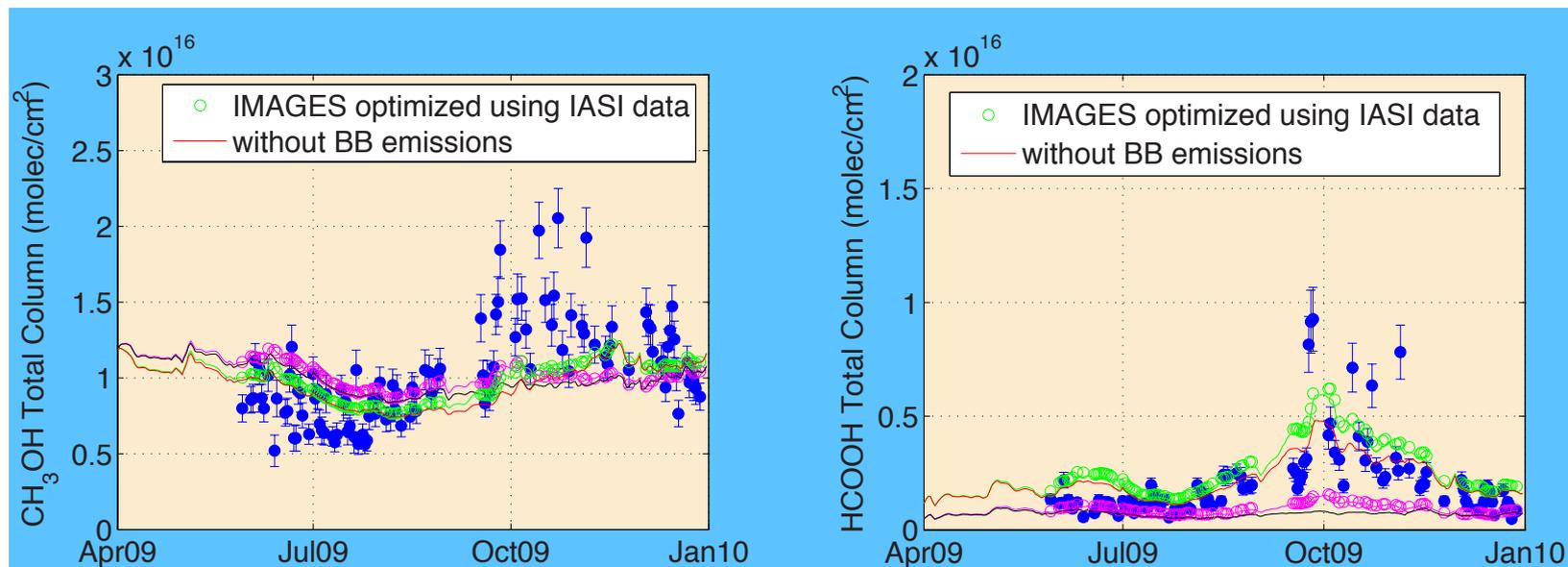


Figure 1: Time-series of daily mean total columns at Reunion Island: CH₃OH (left panel) and HCOOH (right panel). The FTIR data are represented by the blue filled circles, the IMAGESv2 model simulations by the colored lines (magenta for the standard runs; green for the optimized simulations using IASI data), and the model data smoothed with the FTIR averaging kernels with the open circles. The model simulations obtained when the biomass burning (BB) contribution is removed are shown in black for the standard run, and in red for the inversion using IASI data.

HCOOH sources using IASI data greatly improves the agreement with FTIR data during the fire season (Fig. 1, green curve), the contribution of biomass burning given by IMAGESv2 is only minor (red curve compared to green curve). This specific result at Reunion Island seems to disagree with the conclusion based on FTIR measurements that biomass burning is a dominant source of HCOOH at Reunion Island during the August–November period. On the other hand, the FTIR finding is consistent with the study of Paulot et al. (2011). Indeed, they have shown that a good agreement between the HCOOH columns modelled by GEOS-Chem and the FTIR measurements at Reunion Island can be achieved

by assuming that organic aerosol (OA) oxidation generates a diffuse source of formic acid, knowing that the dominant source of OA in the Southern Hemisphere is biomass burning. However, this additional source coming from OA ageing cannot explain the large differences between both models and observations in the Northern Hemisphere, where the additional biogenic source suggested by Stavrakou et al. (2012) seems to be a good candidate for the missing source. Ground-based formic acid FTIR data in the Northern Hemisphere could help for future model investigations.

In conclusion, we have demonstrated in recent papers that

ground-based FTIR measurements of VOCs are very useful for satellite validation and to evaluate the CTMs (missing sources or sinks, dynamical processes) and their input parameters such as emission factors and biomass burning emission inventories. Other parameters such as the fire injection heights or the convective updraft fluxes should also be investigated in future model evaluations. The infrared working group within NDACC offers long time-series measurements of VOCs with a good spatial coverage, to be further exploited by both satellite and model communities.

References

- Duflot, V., Hurtmans, D., Clarisse, L., R'honi, Y., Vigouroux, C., De Mazière, M., Mahieu, E., Servais, C., Clerbaux, C., and Coheur, P.-F.: Measurements of hydrogen cyanide (HCN) and acetylene (C_2H_2) from the Infrared Atmospheric Sounding Interferometer (IASI), *Atmos. Meas. Tech. Discuss.*, **5**, 7567-7586, 2012.
- González Abad, G., Bernath, P. F., Boone, C. D., McLeod, S. D., Manney, G. L., and Toon, G. C.: Global distribution of upper tropospheric formic acid from the ACE-FTS, *Atmos. Chem. Phys.*, **9**, 8039-8047, 2009.
- Jones, N. B., Riedel, K., Allan, W., Wood, S., Palmer, P. I., Chance, K., and Notholt, J.: Long-term tropospheric formaldehyde concentrations deduced from ground-based fourier transform solar infrared measurements, *Atmos. Chem. Phys.*, **9**, 7131-7142, 2009.
- Mahieu, E., Zander, R., Delbouille, L., Demoulin, P., Roland, G., and Servais, C.: Observed trends in total vertical column abundances of atmospheric gases from IR solar spectra recorded at the Jungfraujoch, *J. Atmos. Chem.*, **28**, 227-243, 1997.
- Mahieu, E., Duchatelet, P., Bernath, P. F., Boone, C. D., De Mazière, M., Demoulin, P., Rinsland, C. P., Servais, C., and Walker, K. A.: Retrievals of C_2H_2 from high-resolution FTIR solar spectra recorded at the Jungfraujoch station (46.5°N) and comparison with ACE-FTS observations, *Geophys. Res. Abstr.*, **10**, EGU2008-A-00000, 2008.
- Notholt, J., Toon, G. C., Lehmann, R., Sen, B., and Blavier, J.-F.: Comparison of Arctic and Antarctic trace gas column abundances from ground-based Fourier transform infrared spectrometry, *J. Geophys. Res.*, **102**, 12863-12869, 1997.
- Paton-Walsh, C., Wilson, S. R., Jones, N. B., and Griffith, D. W. T.: Measurement of methanol emissions from Australian wildfires by ground-based solar Fourier transform spectroscopy, *Geophys. Res. Lett.*, **35**, L08810, 2008.
- Paton-Walsh, C., Deutscher, N. M., Griffith, D. W. T., Forgan, B. W., Wilson, S. R., Jones, N. B., and Edwards, D. P.: Trace gas emissions from savanna fires in Northern Australia, *J. Geophys. Res.*, **115**, D16314, 2010.
- Paulot, F., Wunch, D., Crouse, J. D., Toon, G. C., Millet, D. B., DeCarlo, P. F., Vigouroux, C., Deutscher, N. M., González Abad, G., Notholt, J., Warneke, T., Hannigan, J. W., Warneke, C., de Gouw, J. A., Dunlea, E. J., De Mazière, M., Griffith, D. W. T., Bernath, P., Jimenez, J. L., and Wennberg, P. O.: Importance of secondary sources in the atmospheric budgets of formic and acetic acids, *Atmos. Chem. Phys.*, **11**, 1989-2013, 2011.
- Razavi, A., Karagulian, F., Clarisse, L., Hurtmans, D., Coheur, P. F., Clerbaux, C., Müller, J. F., and Stavrou, T.: Global distributions of methanol and formic acid retrieved for the first time from the IASI/MetOp thermal infrared sounder, *Atmos. Chem. Phys.*, **11**, 857-872, 2011.
- Rinsland, C. P., Goldman, A., Murcray, F. J., Stephen, T. M., Pougatchev, N. S., Fishman, J., David, S. J., Blatherwick, R. D., Novelli, P. C., Jones, N. B., and Connor, B. J.: Infrared solar spectroscopic measurements of free tropospheric CO, C_2H_6 , and HCN above Mauna Loa, Hawaii: seasonal variations and evidence for enhanced emissions from the Southeast Asian tropical fires of 1997-1998, *J. Geophys. Res.*, **104**(D15), 18667-18680, 1999.
- Rinsland, C. P., Meier, A., Griffith, D. W. T., and Chiou, L. S.: Ground-based measurements of tropospheric CO, C_2H_6 , and HCN from Australia at 34°S latitude during 1997-1998, *J. Geophys. Res.*, **106**, 20913-20924, 2001.
- Rinsland, C. P., Jones, N. B., Connor, B. J., Wood, S. W., Goldman, A., Stephen, T. M., Murcray, F. J., Chiou, L. S., Zander, R., and Mahieu, E.: Multiyear infrared solar spectroscopic measurements of HCN, CO, C_2H_6 , and C_2H_2 tropospheric columns above Lauder, New Zealand (45°S latitude), *J. Geophys. Res.*, **107**(D14), 4185, 2002.
- Rinsland, C. P., Mahieu, E., Zander, R., Goldman, A., Wood, S., and Chiou, L.: Free tropospheric measurements of formic acid (HCOOH) from infrared ground-based solar absorption spectra: retrieval approach, evidence for a seasonal cycle, and comparison with model calculations, *J. Geophys. Res.*, **109**, 2004.
- Rinsland, C. P., Mahieu, E., Chiou, L., and Herbin, H.: First ground-based infrared solar absorption measurements of free tropospheric methanol (CH_3OH):

- multidecade infrared time series from Kitt Peak (31.9°N, 111.6°W): trend, seasonal cycle, and comparison with previous measurements, *J. Geophys. Res.*, **114**, D04309, 2009.
- Stavrakou, T., Guenther, A., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P.-F., Hurtmans, D., Karagulian, F., De Mazière, M., Vigouroux, C., Amelynck, C., Schoon, N., Laffineur, Q., Heinesch, B., Aubinet, M., Rinsland, C., and Müller, J.-F.: First space-based derivation of the global atmospheric methanol emission fluxes, *Atmos. Chem. Phys.*, **11**, 4873-4898, 2011.
- Stavrakou, T., Müller, J.-F., Peeters, J., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P.-F., Hurtmans, D., De Mazière, M., Vigouroux, C., Deutscher, N. M., Griffith, D. W. T., Jones N., and Paton-Walsh, C.: Satellite evidence for a large source of formic acid from boreal and tropical forests, *Nature Geosci.*, **5**, 26-30, 2012.
- van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., and Arellano Jr., A. F.: Interannual variability in global biomass burning emissions from 1997 to 2004, *Atmos. Chem. Phys.*, **6**, 3423-3441, 2006.
- van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009), *Atmos. Chem. Phys.*, **10**, 2010.
- Vigouroux, C., Hendrick, F., Stavrakou, T., Dils, B., De Smedt, I., Hermans, C., Merlaud, A., Scolas, F., Senten, C., Vanhaelewyn, G., Fally, S., Carleer, M., Metzger, J.-M., Müller, J.-F., Van Roozendaal, M., and De Mazière, M.: Ground-based FTIR and MAX-DOAS observations of formaldehyde at Reunion Island and comparisons with satellite and model data, *Atmos. Chem. Phys.*, **9**, 9523-9544, 2009.
- Vigouroux, C., Stavrakou, T., Whaley, C., Dils, B., Dufлот, V., Hermans, C., Kumps, N., Metzger, J.-M., Scolas, F., Vanhaelewyn, G., Müller, J.-F., Jones, D. B. A., Li, Q., and De Mazière, M.: FTIR time-series of biomass burning products (HCN, C₂H₆, C₂H₂, CH₃OH, and HCOOH) at Reunion Island (21°S, 55°E) and comparisons with model data, *Atmos. Chem. Phys.*, **12**, 10367-10385, 2012.
- Zander, R., Duchatelet, P., Mahieu, E., Demoulin, P., Roland, G., Servais, C., Auwera, J. V., Perrin, A., Rinsland, C. P., and Crutzen, P.J.: Formic acid above the Jungfrauoch during 1985-2007: observed variability, seasonality, but no long-term background evolution, *Atmos. Chem. Phys.*, **10**, 10047-10065, 2010.
- Zhao, Y., Strong, K., Kondo, Y., Koike, M., Matsumi, Y., Irie, H., Rinsland, C. P., Jones, N. B., Suzuki, K., Nakajima, H., Nakane, H., and Murata, I.: Spectroscopic measurements of tropospheric CO, C₂H₆, C₂H₂, and HCN in Northern Japan, *J. Geophys. Res.*, **107**, 4343, 2002.