

LINKING OMI HCHO AND MODIS PRI SATELLITE DATA WITH BVOCs EMISSIONS IN NE SPAIN

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ABSTRACT

Volatile organic compounds (VOCs) play several important roles on tropospheric chemical composition. Biogenic VOCs (BVOCs) are the largest source of NMVOCs (non-methane VOCs), accounting for the release of up to 10% of total C fixed by plants in photosynthesis. As isoprene is often the dominant source of atmospheric formaldehyde (HCHO) detected using satellite sensors, it is often correlated directly to satellite HCHO observations without accounting for other HCHO sources. Here we investigate the importance of quantifying monoterpene emissions when linking remotely sensed HCHO vertical columns to terrestrial BVOCs emissions at four different ecosystems in NE Spain where monoterpene-isoprene emissions ratios are known to be unusually high. Average HCHO yield for present monoterpenes was approximately 29% compared to 45% for isoprene. Including monoterpene HCHO yield contributions in total atmospheric HCHO concentrations improved correlations from R^2 of 0.35 to 0.66 and R^2 of 0.56 to 0.89 when comparing OMI HCHO and MODIS PRI satellite with HCHO field measurements, respectively.

Index Terms— OMI, MODIS, BVOCs, HCHO, forest health, climate change

1. INTRODUCTION

Biogenic volatile organic compounds (BVOCs) are a subset of a diverse collection of atmospheric volatile organic compounds in the troposphere and a major source of uncertainty in our current understanding of plant physiology and ecology [1, 2], vegetation impacts on atmospheric chemistry [3-5], and vegetation feedbacks related to climate change [6-8]. To gain knowledge on these processes, BVOCs must be assessed in space and time, and the tool to do so is remote sensing. The remote sensing of BVOCs

relies on the spectral detection of tropospheric formaldehyde (HCHO) as the principal intermediate product of the oxidation of BVOCs, which, with its short lifetime and primary continental BVOC origin, can be used as a proxy or top-down constraint on local BVOCs emissions [9-11] whose primary atmospheric product is HCHO.

BVOCs are the largest source of NMVOCs contributing 1150 TgC/yr, composed of 44% isoprene, 11% monoterpenes, 22.5% other reactive VOCs and 22.5% other VOCs [12], accounting for approximately 85% of total NMVOCs, with the remainder 13% attributed anthropogenic sources [13] and 3% to fires [14]. This accounts for a release of up to 10% of total C fixed by plants in photosynthesis and can fluctuate greatly depending on plant condition [15]. Not only do BVOCs present a potential contribution to climate change, they are also susceptible to global change and global warming [8, 16]. New evidence suggests that one of the major drivers of an observed increase in BVOCs emissions may be thermotolerance [15, 17]. This could have a positive feedback relationship as BVOCs with climate change. The 2-3 C degree increase in global temperature prediction this century [18] has been calculated to correspond to a 30-45% increase in BVOCs [19].

As isoprene is often the dominant source of atmospheric formaldehyde (HCHO) detected using satellite sensors, it is often correlated directly to satellite HCHO observations without accounting for other HCHO sources. Here we investigate the importance of quantifying monoterpene emissions when linking remotely sensed HCHO vertical columns from OMI to terrestrial BVOCs emissions at four different ecosystems in NE Spain where monoterpene-isoprene emissions ratios are known to be unusually high. We also investigated the potential for MODIS PRI as a correlate for BVOCs emissions because of the intrinsic ecophysiological link between the xanthophyll cycle and temperature and other stress factors related to increases in BVOCs emissions.

Table 1. Formaldehyde (HCHO) percent yields from the oxidation of BVOCs emissions including: isoprene and various monoterpenes (MT) and sesquiterpenes (ST).

| Compound | HCHO Yield |
|-----------------------------------|-------------|
| Isoprene | 0.45 |
| Convertible MT and ST Data | |
| MT: α -Pinene | 0.16 |
| MT: D3-Carene | 0.21 |
| MT: α -Terpinene | 0.078 |
| MT: α -Terpinolene | 0.23 |
| MT: β -Pinene | 0.49 |
| MT: β -Myrcene | 0.74 |
| MT: γ -Terpinene | 0.17 |
| MT: Limonene | 0.19 |
| ST: β -Caryophyllene | 0.42 |
| ST: longifolene | 0.25 |
| Monoterpene average | 0.29 |

2. STUDY SITES AND METHODS

Field measurements were conducted at four sites, each characteristic of a region of NE Spain in campaigns during early spring in April of 2010 and summer in July of 2010 as described by Llusia et al. [20]. The selected measurement sites were Monegros (MOG), Garraf (GAR), Prades (PRA), and Montseny (MSY). Monoterpene (MT) and sesquiterpene (ST) emission rates were measured, listed by the species studied, for each site and hours studied (Tt: *Thymelaea tinctoria*, Qc: *Quercus coccifera*, Qi: *Quercus ilex*, Fs: *Fagus sylvatica*, N = 3 for all species except N = 4 for *Q. ilex*; Ms: Monegros, G: Garraf, P: Prades, M: Montseny). The region of Los Monegros is a mostly flat land ranging from 812 m to 190 m with a continental and arid climate. The sampling location was at 41.79979395, 0.58662290 at 531 m. The dominant vegetation there is composed by *T. tinctoria*, *Genista sp.*, *Rosmarinus officinalis*, *Thymus vulgaris*, *Helichrysum sp.* and *Pinus halepensis*. Garraf is a dry shrubland in Rosmarino-Ericion Natural Park sampled at 41.306941, 1.83860786 at 335 m. The climate of this site is typically Mediterranean. The site suffered big fires in the summers of 1982 and 1994 with the regenerating vegetation covering 50-60% with a maximum height of 70 cm.

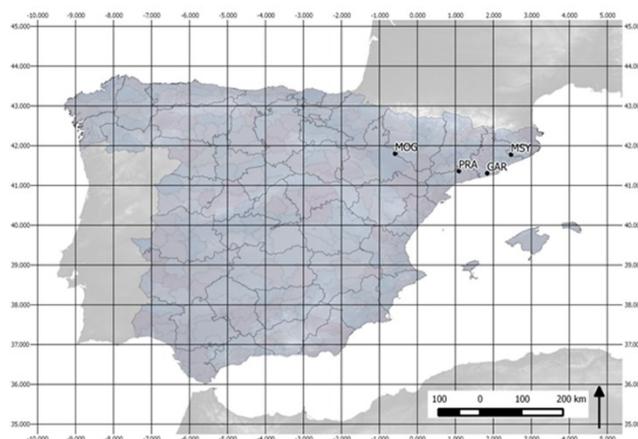
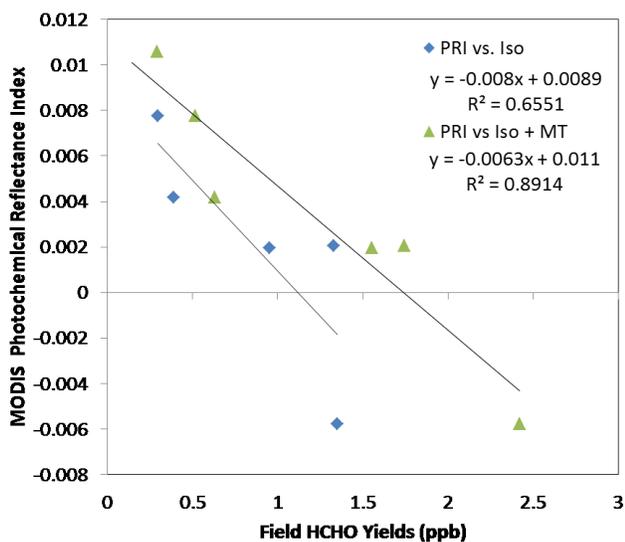
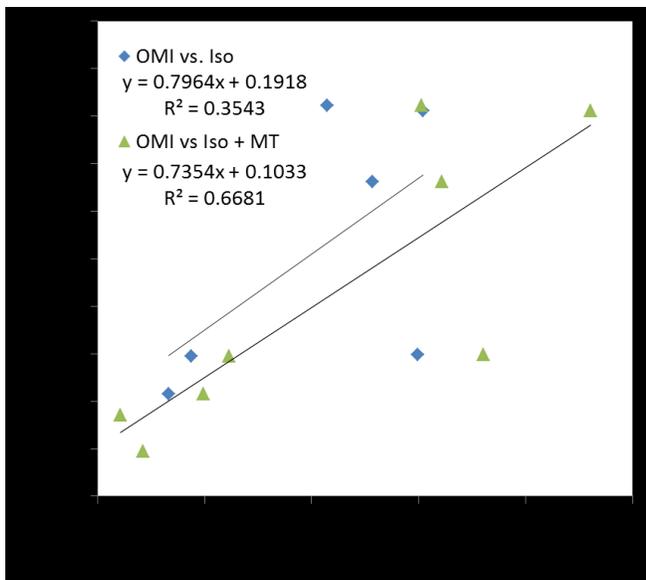


Figure 1. Study site locations for the MONTES data collection (MOS: Monegros, GAR: Garraf, PRA: Prades, MSY: Montseny).

The dominant species at the study site are *Q. coccifera*, *Erica multiflora* L., *Globularia alypum* L., *P. halepensis* L., *R. officinalis* L., and the less abundant *Pistacia lentiscus* L. The sampling location in Prades Mountains was at 41.36089454, 1.09145915, with an elevation of 872 m. The Prades forest is a typical Mediterranean holm oak forest (about 10 m tall), dominated by *Q. ilex* with *Phillyrea latifolia*, *Arbutus unedo*, *Pinus sylvestris*, *Erica arborea*, and *Juniperus oxycedrus*. The Montseny site of study was located within the densely forested of Montseny Natural Park located 25 km from the Mediterranean coast at 41.77592007, 2.46533579 and 1137 m above sea level. The site is covered by deciduous beech forest (about 20-25 m tall trees) *F. sylvatica* with *Ilex aquifolium* and a few patches of *Abies alba*.

The Ozone Monitoring Instrument (OMI) on the EOS AURA satellite was designed to monitor key atmospheric pollutants identified by the U.S. Environmental Protection Agency as posing serious threats to human health and agricultural productivity including HCHO, the primary product of BVOCs [21]. OMI HCHO data was processed and downloaded using GIOVANNI (<http://disc.sci.gsfc.nasa.gov/Giovanni>).

The MODerate Resolution Imaging Spectroradiometer (MODIS) aboard the NASA Terra EOS and Aqua EOS satellites includes 36 spectral bands capable of calculating numerous spectral indices, such as MODIS PRI from reflectance in bands 11(526 – 536 nm) and 12 (546 – 556 nm) as $PRI = (R_{570} - R_{530}) / (R_{570} + R_{530})$.



Figures 2a) OMI HCHO vertical columns compared with field BVOCs HCHO yields of isoprene alone (OMI vs. Iso) and isoprene plus monoterpenes (OMI vs. Iso + MT) and converted to HCHO yield under typical atmospheric conditions using average values of 0.29 for monoterpenes and 0.45 for isoprene; and 2b) MODIS Photochemical Reflectance Index values for an average of 5000 m of each study site compared to field based HCHO yields from isoprene alone (PRI vs. Iso) and isoprene plus monoterpenes (PRI vs. Iso + MT). Field observations are from balloons at approximately 100m altitude taken in April and July over all four sites in Spain

3. RESULTS AND DISCUSSION

Average HCHO yield for present monoterpenes was approximately 29% on average for the measured compounds compared to 45% for isoprene. Including monoterpene

HCHO yield contributions to atmospheric HCHO concentrations improved the correlation (R^2 from 0.3543 to 0.6681) when comparing OMI satellite HCHO with field data. This demonstrates that while isoprene may dominate BVOCs emissions and have a higher percent yield compared to monoterpenes, the inclusion of monoterpenes can significantly improve correlations between satellite estimates of HCHO sources and field BVOCs measurements. Likewise, including monoterpene yield contributions to atmospheric HCHO concentrations improved the correlation (R^2 from 0.6651 to 0.8914) when comparing field data to MODIS PRI satellite-based estimates of photosynthetic light use efficiency.

4. CONCLUSIONS

While more data are needed to better support conclusions based on these results, it appears that the current OMI and MODIS satellite HCHO and PRI products, respectively, are capable of providing estimates of BVOCs, which may be of importance in reducing uncertainties in models of future climate change impacts and feedback mechanisms. In both cases the inclusion of monoterpene HCHO yield contributions provided improvements.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- [1] J. Peñuelas, and J. Llusà, "The complexity of factors driving volatile organic compound emissions by plants," *Biologia Plantarum*, vol. 44, no. 4, pp. 481-487, 2001.
- [2] J. Peñuelas, and J. Llusà, "Linking photorespiration, monoterpenes and thermotolerance in *Quercus*," *New Phytologist*, vol. 155, no. 2, pp. 227-237, 2002.
- [3] A. Arneth, P. A. Miller, M. Scholze *et al.*, "CO₂ inhibition of global terrestrial isoprene emissions: Potential implications for atmospheric chemistry," *Geophysical Research Letters*, vol. 34, no. 18, 2007.
- [4] F. Fehsenfeld, J. Calvert, R. Fall *et al.*, "Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry," *Global Biogeochemical Cycles*, vol. 6, no. 4, pp. 389-430, 1992.
- [5] N. Poisson, M. Kanakidou, and P. J. Crutzen, "Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of

- the global troposphere: 3-dimensional modelling results,” *Journal of Atmospheric Chemistry*, vol. 36, no. 2, pp. 157-230, 2000.
- [6] J. Lathiere, D. Hauglustaine, A. Friend *et al.*, “Impact of climate variability and land use changes on global biogenic volatile organic compound emissions,” *Atmos. Chem. Phys.*, vol. 6, no. 8, pp. 2129-2146, 2006.
- [7] J. Penuelas, and J. Llusia, “BVOCs: plant defense against climate warming?,” *Trends in Plant Science*, vol. 8, no. 3, pp. 105-109, 2003.
- [8] D. E. Shallcross, and P. S. Monks, “New directions: A role for isoprene in biosphere-climate-chemistry feedbacks,” 2000.
- [9] D. S. Abbot, P. I. Palmer, R. V. Martin *et al.*, “Seasonal and interannual variability of North American isoprene emissions as determined by formaldehyde column measurements from space,” *Geophysical Research Letters*, vol. 30, no. 17, pp. 1886, 2003.
- [10] M. P. Barkley, T. P. Kurosu, K. Chance *et al.*, “Assessing sources of uncertainty in formaldehyde air mass factors over tropical South America: Implications for top-down isoprene emission estimates,” *Journal of Geophysical Research: Atmospheres (1984–2012)*, vol. 117, no. D13, 2012.
- [11] P. I. Palmer, D. S. Abbot, T.-M. Fu *et al.*, “Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column,” *Journal of Geophysical Research*, vol. 111, no. D12, 2006.
- [12] A. Guenther, C. N. Hewitt, D. Erickson *et al.*, “A global model of natural volatile organic compound emissions,” *Journal of geophysical research*, vol. 100, no. D5, pp. 8873-8892, 1995.
- [13] J. Olivier, J. Peters, C. Granier, G. Pétron, J.F. Müller,, and a. S. Wallens, *Present and future surface emissions of atmospheric compounds*, Report, 2003.
- [14] T. Stavrakou, J. Müller, I. De Smedt *et al.*, “Evaluating the performance of pyrogenic and biogenic emission inventories against one decade of space-based formaldehyde,” *Atmos. Chem. Phys.*, vol. 9, pp. 1037-1060, 2009.
- [15] J. Llusia, and J. Peñuelas, “Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions,” *American Journal of Botany*, vol. 87, no. 1, pp. 133-140, 2000.
- [16] J. Fuentes, B. Hayden, M. Garstang *et al.*, “New directions: VOCs and biosphere-atmosphere feedbacks,” *Atmospheric Environment*, vol. 35, no. 1, pp. 189-192, 2001.
- [17] T. D. Sharkey, and E. L. Singsaas, “Why plants emit isoprene,” *Nature*, vol. 374, pp. 769, 1995.
- [18] J. T. Houghton, Y. Ding, D. J. Griggs *et al.*, *Climate change 2001: the scientific basis*: Cambridge University Press Cambridge, 2001.
- [19] J. Penuelas, I. Filella, and P. Comas, “Changed plant and animal life cycles from 1952 to 2000 in the Mediterranean region,” *Global Change Biology*, vol. 8, no. 6, pp. 531-544, 2002.
- [20] J. Llusia, J. Peñuelas, A. Guenther *et al.*, “Seasonal variations in terpene emission factors of dominant species in four ecosystems in NE Spain,” *Atmospheric Environment*, vol. 70, pp. 149-158, 2013.
- [21] S. P. Ahmad, P. F. Levelt, P. K. Bhartia *et al.*, “Atmospheric products from the ozone monitoring instrument (OMI).” pp. 619-630.