

Nighttime Chemistry of Biomass Burning Plumes

D.K. Papanastasiou^{1,2}, G.I. Gkatzelis^{1,2}, K. Florou^{1,2}, C. Kaltsonoudis^{1,2}, and S.N. Pandis^{1,2}

¹Institute of Chemical Engineering Sciences (ICEHT), FORTH, Patras, Greece

²Department of Chemical Engineering, University of Patras, Patras, Greece

Keywords: Biomass burning, nighttime oxidation, aging

Presenting author email: dimpapan@iceht.forth.gr

Biomass burning (BB) processes such as wildfires, deforestation and agricultural activities as well as wood burning for residential heating purposes contribute a significant fraction on the total atmospheric burden of organic aerosol (OA) and black carbon (BC) (Bond *et al.*, 2004). Especially, wood burning in fireplaces and woodstoves, is a major air pollution source in wintertime for the region of Greece, in the last few years (Paraskevopoulou *et al.*, 2014). Biomass burning aerosols not only have a tremendous impact on human health but can also affect Earth's climate due to the presence of BC and of either light absorbing or light reflecting organic material. Constraining the effects of biomass burning, especially on climate, requires a detailed knowledge of gas and particulate emissions during the combustion process as well as the physicochemical transformation of biomass burning plumes in the atmosphere.

Previous studies on biomass burning plume daytime chemistry have shown formation of secondary organic aerosol (SOA) due to VOC oxidation with OH, accompanied with a rapid transition of biomass burning organic aerosol (BBOA) to relatively more aged OA within a few hours of photochemical oxidation (Cubison *et al.*, 2011). Recent field campaigns indicate that there is also important processing of BBOA and co-emitted VOCs during the night (Crippa *et al.*, 2013 and Bougiatioti *et al.*, 2014). In these campaigns, aerosol mass spectrometry and source apportionment techniques identified two components of OA originating from biomass burning: one similar to unprocessed BBOA and one more aged BBOA (higher O:C ratio). Although, the nighttime field observations clearly support the existence of aged BBOA, the atmospheric processes that lead to the transformation of fresh biomass burning OA are yet to be elucidated.

In this work, the nighttime chemistry of residential biomass burning vapors and particles was examined in a series of smog chamber experiments. In all the experiments, a suite of instrumentation was used for the characterization of both the gas (PTR-MS, O₃ and NO_x analyzers) and particulate phase (HR-ToF-AMS, MAAP and SMPS). A typical woodstove was used for controlled burns of mixed oak and beech wood. In the first set of experiments, a small fraction of biomass burning smoke was directed and diluted into a 10 m³ chamber prefilled with clean air. Experiments were performed at two different T and RH conditions (T=25 C, RH=20% and T=17 C, RH=60%). During the first stage of measurements, the initial biomass burning chemical composition in both the gas and particulate

phase was characterized without any alteration of its chemical environment. In the second set of experiments, the diluted biomass burning emissions were exposed to various mixing ratios of NO₂ and O₃ similar to those found in the nighttime atmosphere, so as to evaluate the significance of nighttime oxidants such NO₃ radicals and O₃.

The initial characterization of "fresh" biomass burning plume was extensively compared to that measured during various field and chamber campaigns. The emission factors for major VOCs (oxygenated hydrocarbons, terpenes and aromatics) were found to compare well with literature values. Moreover, BBOA AMS mass spectra were found to be in very good agreement with reported ones from several field campaigns. Finally, analysis of BBOA mass spectra revealed that aged BBOA is not co-emitted during the initial burning phase.

In the experiments in which the biomass burning emissions were exposed to nighttime oxidants (NO₃ radicals and O₃) significant changes to OA properties were observed. More specifically, an enhancement of OA ranging from 10% to about a factor of 2 was measured, depending on the conditions of the experiments (oxidants and VOC concentration). OA was found to increasingly oxidize upon NO₃/O₃ exposure, as derived by changes to the fraction of *m/z* 44 (up to 50%) and O:C ratio (up to 40%). Box model simulations showed that monoterpenes, present in the biomass burning plume, react primarily with O₃ (70-80%) and to a lesser extent with NO₃ radicals (20-30 %) under the conditions of these experiments. Finally, the fraction of levoglucosan, a commonly used biomass burning tracer, was found to decrease (up to 50%) mostly due to SOA formation that increases total OA and due to its evaporation in the gas phase given its semivolatile nature. Finally, the atmospheric implications of this work as well as its connection with field measurements of BBOA nighttime processing are discussed in detail.

This research was supported by the Hellenic ESF-NRSF ARISTEIA grant ROMANDE

Bond, T.C., *et al.* (2004), *J. Geophys. Res.*, **109**, D14203
Paraskevopoulou, D., *et al.* (2014), *Atmos. Chem. Phys.*, **14**, 13313

Cubison, M. J., *et al.* (2011), *Atmos. Chem. Phys.*, **11**, 12049

Crippa, M., *et al.* (2013), *Atmos. Chem. Phys.*, **13**, 961

Bougiatioti, A., *et al.* (2014), *Atmos. Chem. Phys.*, **14**, 4793