Chemical characterization of laboratory-generated tar ball particles

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Atmospheric tar balls (TBs) are a specific particle type of carbonaceous aerosol emitted during biomass burning. These particles belong to the family of atmospheric *brown carbon* (BrC), as they absorb light in the visible range of the solar spectrum and they are distinctly different from BC in morphology. Albeit TBs are important constituents of biomass burning plumes, very little is known about the chemical composition of these particles, because in biomass smoke TBs coexist with various other particle types (e.g., organic particles with inorganic inclusions, soot) from which they cannot be physically separated; thus, their chemical properties have been examined only by single particle analysis techniques such as transmission electron microscopy – energy-dispersive X-ray spectroscopy (TEM-EDS). According to the TEM-EDS investigations TBs are amorphous, spherical particles, present usually as individual stand-alone particles. Their sizes range from 30 to 500 nm in geometric diameter. TBs are refractory particles as they can withstand the high-energy electron beam of the TEM. TBs contain high amount of carbon, minor amount of oxygen, the average C/O molar ratio being about 10 based on TEM-EDS (Pósfai, *et al*, 2004).

In this work the chemical properties of pure TB particles generated in the laboratory without the concurrent emission of other combustion products, were investigated by elemental analysis (EA), pyrolysis-gas chromatography – mass spectrometry (py-GC-MS), Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy.

Tar balls were generated from the aqueous phases of the dry distillate prepared from hardwood (turkey oak, black locus) and softwood, (Norway spruce) similarly to that described by Hoffer et al. (2016). The samples were collected onto different substrates (quartz filter, aluminium foil and copper TEM grid). Simultaneously with the sampling the optical parameters (scattering- and absorption coefficient at 3 different wavelengths) of the generated particles were measured to follow the generation procedure (Hoffer *et al*, 2016).

According to results of the TEM measurements the morphological features and the chemical composition of the generated TB particles were similar to those characteristic for atmospheric TBs. The results of the elemental analysis of bulk TB samples showed that the elemental composition of the TB particles generated from the three different tree species were similar to each other and to that characteristic for atmospheric TBs. The C/O, C/H and C/N molar ratios ranged from 9.14 to 10.62 (average: 10.13), from 1.71 to 1.96 (average: 1.84), and from 23.53 to 54.89 (average: 36.70), respectively. The chemical structures of the TB particles collected onto quartz filters were examined by py-GC-MS. Lignin-derived phenolic, aromatic, heterocyclic aromatic components, and bi- or tricycle polycyclic aromatic hydrocarbons (PAHs) were identified in the chromatograms. These PAHs were also identified in higher amounts in soot from wood burning (Song and Peng, 2010). The FT-IR measurements indicated that a significant fraction of the oxygen atoms of the TBs can be found in hydroxyl and keto functional groups. The spectra of TBs were very similar to spectra of lignocellulosic substances (Yang *et al*, 2007). While the aqueous phases of tars were Raman inactive, the appearance of G (characteristic for graphene structures) and D bands (characteristic for structural disorder in graphene structures) in the TB's Raman spectra indicated the presence of short-range order in molecular structures.

Our results demonstrated that the chemical properties of tar balls bear the characteristic chemical signature of soot but also that of pyrolysed wood.

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