Investigation of Artificially Generated and Ambient Carbonaceous Particulate Matter

Summary of PhD Thesis

By

Máté Dániel Pintér

Supervisor

Dr. Tibor Ajtai, PhD

senior research fellow

Doctoral School of Environmental Sciences

Department of Optics and Quantum Electronics

Faculty of Science and Informatics

University of Szeged

Szeged

2018

1. INTRODUCTION

Atmospheric aerosol is in the focus of scientific interest due to its impact on climate human health as well as issues related to its legal regulation. Airborne particles can force climate directly (scattering and absorbing solar radiation) and indirectly (participating in cloud formation processes). Direct scattering of solar radiation has cooling (negative forcing) while absorption has heating impact (positive forcing). Recently, more and more attention has been focused on carbonaceous particulate matter (CPM) and especially on its light absorbing fraction. Light absorbing carbonaceous aerosol components (LAC) have the second highest positive radiative forcing following. Radiative forcing by aerosol is estimated with huge uncertainty. Indirect (cloud) forcing associated to aerosols is currently the largest factor of uncertainty in climatic models.

Uncertainty generally arises from two factors. Firstly, inherent properties of carbonaceous particles are primarily determined by the initial burning conditions and fuel type. Secondly, aerosol properties are significantly affected by physical and chemical interactions between aerosol particles and their ambience. These processes are generally referred to as atmospheric aging. Therefore, interpretation of data acquired during immission measurements is still limited. Simultaneous measurement of aerosol parameters utilizing combined online and offline methods among well-controlled laboratory circumstances and at various field locations could decrease limitations. Another difficulty is the lack of a generally accepted reference material that can model the complex properties of atmospheric CPM. There are instruments that can provide model carbonaceous aerosol that mimic the properties of fossil fuel and biomass burning emitted aerosol. However, neither makes it possible to investigate the most relevant CPM properties independently from each other in the function of factors influencing particle formation.

Urban CPM dominantly originates from various anthropogenic emission sources. During the winter, traffic and household burning (mostly for heating) were found the be the most significant sources of emission. Diesel emitted carbonaceous particulate matter (DPM) is classified as carcinogenic to humans by the World Health Organization (WHO). DPM has also recently been found to have a significant ecotoxicological impact as well. Increasing diesel engine standards and diesel exhaust aftertreatment systems like diesel particulate filter (DPF), exhaust gas recirculation (EGR) and diesel oxidation catalysts (DOC) are expected to decrease associated health risks. As opposed to that the toxicological nature of emission from domestic burning has only been getting recognized recently. Working out solution strategies for regulating domestic particulate emission is still a challenge to be faced in the future.

I joined MTA-SZTE Research Group on Photoacoustic Spectroscopy in 2011 as a graduate student. Aerosol laboratory of the research group and adjunct scientific infrastructure of the University of Szeged Faculty of Natural Sciences and Informatics provides a unique opportunity for the investigation of the complex physical and chemical features of atmospheric and artificially generated carbonaceous aerosol even on an international level.

2. SCIENTIFIC OBJECTIVES

My goal was to study size distribution, morphology and microstructure of artificially generated model as well as real diesel emitted CPM. I was aiming to investigate the impact of various conditions of formation and fuel types on the characteristics parameters of emitted CPM. My further goal was to study the correlations between the online measured optical absorption properties and the offline studied chemical and toxicological potential of urban CPM. With respect to that I was also aiming to assess the applicability of the AAE as a first-screening indicator of CPM toxicity.

Accordingly, I assigned the following sub-tasks:

1. Characterization of the size distribution, morphology and microstructure of model carbonaceous aerosol particles generated by laser ablation of a high purity graphite sample in the function of generation parameters.
2. Investigation of the size distribution, total number and volume concentration as well as the morphology and microstructure of diesel emitted particulate matter in the function of engine operating conditions in case of blends of commercially available diesel and biofuels.
3. Studying the thermal evolution of diesel emitted particulate matter (the ratio of constituents with distinct thermal stability found in diesel exhaust) using in in-house developed thermal adsorption unit (thermodenuder).
4. Determining the diurnal variation of a wide range of parameters measured by offline and online methodologies describing atmospheric carbonaceous particulate matter and co-emitted gaseous constituents. Based on their diurnal variation, investigating the correlation between offline determined chemical and toxicological properties and online measured microphysical and spectral features of urban CPM. Assessing the possibility of first-screening the toxicological potential of CPM based online measurement of its spectral response.

3. EXPERIMENTAL METHODS

3.1. Online measurements

- **Optical absorption** of studied aerosols was determined by the previously in-house developed Four Wavelength Photoacoustic Spectrometer (4λ-PAS). The operational wavelengths of the instrument are 1064, 532, 355 and 266 nm.
- A Scanning Mobility Particle Sizer (SMPS equipped with a Vienna-type DMA+CPC, Grimm Aerosol Technik GmbH & CO.) was used to measure aerosol **size distribution** and **total number concentration** in the size range of 10.1-1093 nm. During field measurements, the SMPS was combined with a Grimm Aerosol Technik GmbH & CO. Portable Aerosol Spectrometer is an Optical Particle Counter (OPC) measuring size distribution in the size range of 0.25-32 μm.
- **Mass concentration** was determined by a Tapered Element Oscillating Microbalance (TEOM) manufactured by Thermo Fischer Scientific during laboratory measurements. In case of field measurements, mass concentration was measured by a Met One Instruments BAM 1020 beta attenuation mass monitor.
- **CO, NO_x and BTEX concentration** was determined by a Syntech Spectras GC955 Gas Chromatograph (Synspec b.v.) as supplementary parameters supporting the discussion of our field measurement.

3.2. Offline methods

- **Morphology** and the **microstructure** of the aerosol particulates were determined by Transmission Electron Microscopy (TEM, FEI Tecnai G2 20 X-Twin) and Raman Spectroscopy (Thermo Scientific DXR Raman Microscope).
- **Elemental carbon (EC), organic carbon (OC) and total carbon (T**C) (hereafter quoted as TC_{Sunset}) concentrations were determined by a thermo-optical Semi Continuous OCEC Analyzer (Sunset Laboratory Inc.) using protocol EUSAAR_2. Total carbon (TC) concentration was also measured by a Zellweger Analytics Astro 2100 TOC Analyzer by the EGA method (hereafter quoted as $TC_{Zellweger}$) from the filter extracts.
- **Levoglucosan (LG)** was determined by an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer extracted filter collected air samples.
- The **concentration of PAH compounds** was measured by High Performance Liquid Chromatography (HPLC).
- The *Vibrio Fischeri* bioluminescence bioassay was applied for determining the **ecotoxicity (EC50)** of filter collected PM samples following the protocol as described in the ISO 21338:2010 standard.

4. SUMMARY

During my doctoral research I studied size distribution, morphology and microstructure of artificially generated model as well as real diesel emitted CPM. I investigated the impact of various burning conditions on the characteristics parameters of emitted CPM. I also studied the correlations between the online measured optical absorption properties and the offline studied chemical and toxicological potential of urban CPM. I assessed the applicability of the AAE as a first-screening indicator of CPM toxicity.

New scientific results summarized in thesis statements

T1. I investigated the size distribution, morphology and microstructure of CPM generated from a graphite target by laser ablation. This CPM generating setup ensures a unique possibility for evolving particles with various microphysical parameters and morphology. The tunable parameters of the setup are fluence of laser excitation, flow rate and composition of carrier gas in the ablation chamber. Each parameter can be independently controlled. Generating parameters can model temperature of ignition, physical aging and occurring atmospheric processes, respectively. I experimentally proved that generated carbonaceous particulate matter models real atmospheric soot well.

T2. I characterized particle emission from a heavy-duty diesel engine fuelled with blends of commercial diesel and biofuel (fatty acid methyl ester, FAME). The four investigated fuel blends were pure diesel (B0), 25% FAME (B25), 75% FAME (B75) and pure FAME (B100). I investigated diesel emission at three selected standard engine operating conditions (from idle mode to high engine load). The results of my measurements verified that diesel emitted particulate matter has lognormal size distribution in the accumulation mode (CMD of circa 100 nm) among all measurement conditions. Emitted number and volume concentration was found to decrease in the function of engine load. Blending rate of FAME did not linearly affect emitted number and volume concentration. I measured the smallest emitted concentration in case of B75 regarding all operating conditions. This finding shows that developing new composition fuels (e.g. with higher biofuel content) could help further reduce particulate emission and fulfil tightening emission standards.

T3. I investigated the thermal evolution of diesel emitted particulate matter by posterior temperature treatment of the diesel exhaust at three temperatures using an in-house developed low-flow thermodenuder (50°C, 120°C and 250°C). During the first temperature transition (50-120°C), I observed a significant decrease in number and volume concentrations while no remarkable shift of the peak position of the size distribution curves. I proved that this is due to the evaporation of droplets formed by homogenous condensation and volatile matter previously adsorbed on the surface of soot particles as well as the pyrolysis of non-soot constituents in the exhaust. During the second temperature transition (120-250°C), I observed further decrease in total volume concentration and structural changes in size distribution regarding all engine conditions and fuel types. In idle mode, total number concentrations did not show significant further decrease in case of all fuel types. Curiously, at higher engine loads, as opposed to pure fuels (B0 and B100), total number concentration increased during the second temperature transition in case of fuel blends (B25 and B75). I demonstrated that this phenomenon can be explained by the fragmentation of aggregates governed by thermal energy.

T4. I investigated the diurnal variation and the correlations between the physical, chemical properties and the toxicological potential of atmospheric carbonaceous particulate matter (CPM) during a 2-month field measurement campaign carried out under urban wintry condition at two locations. Optical and microphysical features including optical absorption, light scattering, size distribution and mass concentration were measured using online state-of-the-art instrumentation. Filter samples were collected for offline chemical and toxicological analyses (concentration of PAH, BTEX compounds, total carbon (TC), organic carbon (OC), levoglucosan (LG) and ecotoxicity) with 6-hour time resolution. I found weak to moderate correlations between ecotoxicity and the optical, microphysical and chemical characteristics of CPM suggesting that CPM has remarkable ecotoxicological potential. I found moderate correlation between ecotoxicity determined by the Vibrio Fisheri bioluminescence bioassay and the wavelength dependence of optical absorption (AAE) determined by online aerosol phase photoacoustic measurements. I demonstrated that besides being a chemically and source selective parameter, AAE could also be a possible indicator for first screening the toxicological potential of CPM.

SCIENTIFIC ACTIVITY

Scientific articles related to thesis statements:

T1. Ajtai, T., Utry, N., **Pintér, M.**, Kiss-Albert, G., Puskás, R., Tápai, Cs., Kecskeméti, G., Smausz, T., Hopp, B., Bozóki, Z., Kónya, Z., and Szabó, G. (2015). Micro-physical properties of carbonaceous aerosol particles generated by laser ablation of graphite target. Atmos. Meas. Tech 8: 1207-1215.

IF:2.929

Number of independent citations: 0

T2-T3. Ajtai, T., **Pintér, M**., Utry, N., Kiss-Albert, G., Gulyás, G., Pusztai, P., Puskás, R., Bereczky, Á., Szabados, G., Szabó, G., Kónya, Z., Bozóki, Z. (2016) Characterisation of diesel particulate emission from engines using commercial diesel and biofuels, Atmospheric Environment, Volume 134, June 2016, Pages 109–120.

IF: 3.281

Number of independent citations: 4

T4. **Pintér, M**., Utry, N., Ajtai, T., Kiss-Albert, G., Jancsek-Turóczi, B., Imre, K., Palágyi, A., Manczinger, L., Vágvölgyi, Cs., Horváth, E., Kováts, N., Gelencsér, A., Szabó, G., Bozóki, Z. (2017). Optical Properties, Chemical Composition and the Toxicological Potential of Urban Particulate Matter. Aerosol and Air Quality Research, 17, 1415-1426.

IF: 2.606

Number of independent citations: 1

Conference posters and presentations related to the thesis statements:

Pintér, M., Kiss-Albert, G., Utry, N., Ajtai, T., Szabó, G., Bozóki, Z.. Investigating the Source Dependence of Aethalometer Correction Factors Using an In-House Developed Multi-Wavelength PhotoAcoustic Spectrometer. AAAR 2017 Raleigh NC USA

Pintér M., Kiss-Albert G., Utry N., Ajtai T., Szabó G., Bozóki Z. Légköri aeroszol complex mikrofizikai és spektrális tulajdonságainak vizsgálata téli városi környezetben. Tavaszi Szél 2017, Miskolc, Hungary

Pintér, M., Utry, N., Gulyás, G., Kiss-Albert, G., Ajtai, T., Szabó, G., Bozóki, Z. A thermodenuder assisted dual-wavelength dual cell photoacoustic aerosol analyser with enhanced source apportionment capability. European Aerosol Conference 2016, Tours, France

Ajtai, T., Utry, N., **Pintér, M.**, Kiss-Albert, G., Szabó, G., Bozóki, Z. Thermal analysis of diesel emitted particulate matter. European Aerosol Conference 2016, Tours, France

Utry, N., **Pintér, M.**, Ajtai, T., Kiss-Albert, G., Palágyi, P., Manczinger, L., Vágvölgyi, Cs., Imre, K., Jancsek-Túróczi, B., Gelencsér, A., Szabó, G., Bozóki, Z. Correlations between the toxicity and optical properties of atmospheric aerosol measured by self-developed photoacoustic and supplementary instrumentation. European Aerosol Conference 2016, Tours, France

Ajtai, T., **Pinter, M.**, Utry, N., Kiss-Albert, G., Palágyi, A., Manczinger, L., Vágvölgyi, CS., Szabó, G., Bozóki, Z. On the possibility of real time air quality and toxicology assessment using multiwavelength photoacoustic spectroscopy. EGU 2016, Vienna, Austria,

Ajtai, T., **Pinter, M.**, Utry, N., Kiss-Albert, G., Palágyi, A., Manczinger, L., Vágvölgyi, CS., Szabó, G., Bozóki, Z. On the possibility of real time characterisation of ambient toxicity using multi-wavelength photoacoustic instrument. ICAST 2016, Lisbon, Portugal

Ajtai, T., **Pintér, M.**, Utry, N., Kiss-Albert, G., Gulyás, G., Bereczky, Á., Szabados, Gy., Bozóki, Z., Szabó, G. Thermal evolution and dynamic changes in diesel emission. EAC 2015. Milan, Italy

Ajtai, T., Utry, N., **Pintér, M**., Szabados, Gy., Bereczky, Á., Kiss-Albert, G., Gulyás, G., Bozóki, Z., Szabó, Gr. Dízel korom aeroszolok karakterizálása: A motorterhelés és a kipufogógáz hőmérsékletének hatása a méreteloszlásra. MAK 2015, Szeged, Hungary.

Ajtai, T., Utry, N., **Pintér, M.**, Kecskeméti, G., Smausz, T., Hopp, B., Bozóki, Z., Szabó, G. Generation and characterization of laser induced carbon particles. IAC 2014. Busan, Korea

Pintér, M., Ajtai, T., Utry, N., Bozóki, Z., Szabó, G. Mesterséges és légköri korom aeroszolok optikai abszorpciós tulajdonságainak vizsgálata saját fejlesztésű négy-hullámhosszú fotoakusztikus spektrométerrel. A „Kvantumelektronika 2014: VII. Szimpózium a hazai kvantumelektronikai kutatások eredményeiről" és a Modern Fényforrások és Alkalmazásaik workshop. BME 2014. november 28, Budapest, Hungary.

Ajtai, T., Utry, N., **Pintér, M.**, Bozóki, Z., Szabó, G. Generation and characterization of laser induced carbon particles. Tavaszi szél 2014, Debrecen, Hungary.

Ajtai, T., Utry, N., **Pintér, M.**, Bozóki, Z., Szabó, G. Lézergenerált koromaeroszolok előállítása és karakterizálása. Magyar Aeroszol konferencia 2013. Debrecen, Hungary.

Other relevant scientific articles in the topic:

Pintér, M., Ajtai, T., Kiss-Albert, G., Kiss, D., Utry, N., Janovszky, P., Palásti, D., Smausz, T., Kohut, A., Hopp, B., Galbács, G., Kukovecz, Á., Kónya, Z., Szabó, G., Bozóki, Z. (2018). Thermo-optical properties of residential coals and combustion aerosols. Atmospheric Environment, 178, 118-128.

IF.: 3.629

Smausz, T., Kondász, B., Gera, T., Ajtai, T., Utry, N., **Pintér, M.**, Kiss-Albert, G., Budai, J, Bozóki, Z., Szabó, G., Hopp, B. (2017). Determination of UV–visible–NIR absorption coefficient of graphite bulk using direct and indirect methods. Applied Physics A, 123(10), 633.

IF:1.455

Utry, N., Ajtai, T., **Pintér, M.**, Illés, E., Tombácz, E., Szabó, G., Bozóki, Z. (2017). Generation and UV-VIS-NIR spectral responses of organo-mineral aerosol for modeling soil derived dust. Atmospheric Environment, Volume 152, March 2017, Pages 553–561.

IF: 3.459

Simon, K. A., Ajtai, T., Gulyás, G., Utry, N., **Pintér, M.**, Szabó, G., Bozóki, Z. (2017). Accuracy assessment of aerosol source apportionment by dual wavelength photoacoustic measurements. Journal of Aerosol Science, Volume 104, pp 10-15.

IF: 2.278

Ajtai, T., Utry, N., **Pintér, M.**, Major, B., Bozóki, Z., & Szabó, G. (2015). A method for segregating the optical absorption properties and the mass concentration of winter time urban aerosol. Atmospheric Environment, 122, 313-320.

IF:3.281

Utry, N., Ajtai, T., **Pintér, M.**, Tombácz, E., Illés, E., Bozóki, Z., & Szabó, G. (2014). Mass specific optical absorption coefficients of mineral dust components measured by a multi wavelength photoacoustic spectrometer. Atmos. Measur. Tech. Dis, 7, 9025-9046.

IF: 2.929

Utry, N., Ajtai T., Smausz Kolumbán, T., Kecskeméti G., Tápai Cs., **Pintér M.**, Hopp B., Bozóki Z. (2014). Lézergenerált korom-aeroszolok fotoakusztikus vizsgálata. Fizikai Szemle. 233-236.

Utry, N., Ajtai, T., Filep, Á., **Pintér, M.**, Török, Z., Bozóki, Z., & Szabó, G. (2014). Correlations between absorption Angström exponent (AAE) of wintertime ambient urban aerosol and its physical and chemical properties. Atmospheric environment, 91, 52-59.

IF: 3.281

Utry, N., Ajtai, T., **Pintér, M.**, Bozóki, Z., & Szabó, G. (2014). Wavelength-Dependent Optical Absorption Properties of Artificial and Atmospheric Aerosol Measured by a Multi-Wavelength Photoacoustic Spectrometer. International Journal of Thermophysics, 35(12), 2246-2258.

IF: 0.963

Filep, Á., Ajtai, T., Utry, N., **Pintér, M. D.**, Nyilas, T., Takács, S., Máté, Zs., Gelencsér, A., Hoffer, A., Schnaiter, M., Bozóki, Z., Szabó, G. (2013). Absorption spectrum of ambient aerosol and its correlation with size distribution in specific atmospheric conditions after a red mud accident. Aerosol and Air Quality Research, 13(4).

IF: 2.664

Utry, N., Ajtai, T., Filep, Á., **Pintér, M. D.**, Hoffer, A., Bozoki, Z., & Szabó, G. (2013). Mass specific optical absorption coefficient of HULIS aerosol measured by a four-wavelength photoacoustic spectrometer at NIR, VIS and UV wavelengths. Atmospheric environment, 69, 321-324.

IF: 3.062