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Optical Properties, Chemical Composition and the Toxicological Potential of Urban Particulate Matter

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ABSTRACT

This paper discusses the diurnal variation and the interdependences between the physical, chemical and toxicological characteristics of atmospheric carbonaceous particulate matter (CPM) and co-emitted gaseous components. Measurements were carried out at two different urban sites during a 2-month period. On-line measured parameters were optical absorption coefficients (OAC), total number concentration (TNC), mass concentration of CPM and the concentration of gaseous species (CO, NO_x and BTEX). Off-line analyses were carried out on filters collected with 6-hour time resolution. The concentrations of elemental carbon (EC), organic carbon (OC), total carbon (TC), levoglucosan (LG) and polycyclic aromatic hydrocarbons (PAH) were determined. The ecotoxicity of CPM was assessed by the *Vibrio Fischeri* marine bioluminescence inhibition bioassay (ISO 21338:2010). We found ($r > 0.498$) positive and wavelength dependent correlation between the CPM related parameters based on optical response (OAC, AAE) and thermal stability (TC, EC, OC, OC/TC). We also revealed weak ($r = 0.309$) or moderate ($r = 0.448$) correlation between the AAE and the ecotoxicity data indicating that carbonaceous fraction of the ambient particulate matter has ecotoxicological impact. Based on the determined correlations, we propose the applicability of the AAE determined by multi wavelength photoacoustic measurements as a possible candidate for first-screening the toxicological impact of optically active carbonaceous ambient particulate matter. The strengths and the limitations of this methodology are both discussed here.

Keywords: Aerosol Angström Exponent; Ecotoxicity; Photoacoustic spectroscopy; Polycyclic aromatic hydrocarbons.

INTRODUCTION

The importance of investigating atmospheric carbonaceous particulate matter (CPM) has recently gained widespread recognition. As a result of its optical activity, CPM is thought to be the second most important driver of global warming following CO₂ (Bond *et al.*, 2013). In addition, the major uncertainties of radiative forcing calculations are also linked to this component (Penner *et al.*, 2001; Schwartz, 2004; Lack *et al.*, 2006; Solomon *et al.*, 2007).

It is generally accepted that CPM poses a serious risk to both earthly ecosystems and human health. Several epidemiological studies have demonstrated that exposure

to carbonaceous particulate matter (CPM) can lead to the development of pulmonary malfunctions, respiratory symptoms, cardiovascular diseases and increased hospital admission (Dockery *et al.*, 1993; Schwartz *et al.*, 1994; Pope *et al.*, 2002; Czövek *et al.*, 2012; Longhin *et al.*, 2016; Landkocz *et al.*, 2017). Diesel engine exhaust has been classified as carcinogenic to humans (Group 1) by the World Health Organization (WHO) International Agency for Research on Cancer (IARC) (IARC, 2012). In addition, particulate matter from vehicle exhaust has been found to have ecotoxicological effects (Lin and Chao, 2002; Isidori *et al.*, 2003; Papadimitriou *et al.*, 2008; Vouitsis *et al.*, 2009). In the long run, the use of diesel particulate filters (DPF) are expected to provide solution for decreasing the health risks associated with diesel exhaust. The significance of the toxicological impact of biomass burning emission is getting more and more recognized, however, its regulation is a challenge to be faced in the future (Muala *et al.*, 2014;

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Martinsson et al., 2015; Sigsgaard et al., 2015).

The toxicity of CPM depends on its physicochemical properties (size, morphology, chemical composition, etc.), thus, on its emitting sources (de Kok et al., 2006; Filep et al., 2016; Longhin et al., 2016). The fine (PM_{2.5}) and especially the ultrafine (PM_{0.1}) size fraction have been shown to have the highest toxicity (Tokiwa et al., 1980; Pagano et al., 1996; Cerna et al., 2000; Buschini et al., 2001; Kawanaka et al., 2004; de Kok et al., 2006). Due to their large specific surface, fine particles have a huge capacity for adsorbing different carcinogenic and mutagenic compounds like polycyclic aromatic hydrocarbons (PAH) and heavy metals (Hayakawa et al., 1995; Schnelle et al., 1995; Kawanaka et al., 2002). Toxicological studies have also recently shown that the oxidative properties of certain aerosol constituents like transition metals, organic compounds and reactive oxygen species (ROS) have significant cell-damaging impact (Donaldson et al., 2002; Li et al., 2009). Fine aerosol particles are also able to reach the pulmonary alveoli acting as transporters of toxic compounds.

In general, CPM originates from miscellaneous combustion processes. Among wintry urban conditions - when photochemical and biological activities are negligible - the two dominant sources of CPM are traffic and domestic heating (Sandradewi et al., 2008a, b; Favez et al., 2009; Ajtai et al., 2015). Also, CPM dominates the ultrafine size fraction that possesses the largest toxicity per unit mass (Endo et al., 2003; Sardar et al., 2005; US Environmental Protection Agency, 2005; Kennedy, 2007).

Generally, the health impacts of PM are studied by off-line toxicological assessments carried out on filter collected samples. Ecotoxicity of PM has been most often determined by the *Vibrio fischeri* bioluminescence inhibition bioassay. It is a good indicator of the metabolic activity of an organism as bioluminescence is directly linked to respiratory activity. In addition, due to its short exposure time and automatic test protocols, the *V. fischeri* bioluminescence bioassay can serve the purpose of screening the toxicological potential of PM (reviewed by Kováts and Horváth, 2016). A new test protocol was issued in 2010 as an ISO standard (ISO 21338:2010: Water quality - Kinetic determination of the inhibitory effects of sediment, other solids and coloured samples on the light emission of *Vibrio fischeri* /kinetic luminescent bacteria test/). The kinetic measurement makes possible to test solid samples in suspension, eliminating false toxicity readings caused by turbidity. The method has been further developed for assessing the toxicity of ambient particulate matter using a direct contact between PM and test bacteria (Kováts et al., 2012). Its sensitivity and applicability was verified in ecotoxicity assessment of urban aerosol (Turóczy et al., 2012) and diesel emissions (e.g., Kováts et al., 2013).

Most toxicology tests are ex-situ and can only provide information about air quality with considerable time lag. Samples are usually collected with 24 h time resolution. That way, the daily variation of particulate toxicity and the relative contribution of emitting sources remain obscure in most cases (Cerna et al., 2000; Buschini et al., 2001; Kawanaka et al., 2004; de Kok et al., 2006; Roig et al., 2013).

Although there are numerous studies particularly focusing on the chemical or toxicological properties of ambient particulate matter, our knowledge regarding the relationship between the two is still not adequate (de Kok et al., 2005). Therefore, developing filter-free and real time methods to investigate the interdependence between the toxicological and the microphysical features of ambient aerosol is a highly current issue in air quality research today.

As the optical properties and the toxicological potential of CPM each depend (among others) on chemical composition, the recently discovered link between the absorption spectrum quantified its wavelength dependency - i.e., *Absorption Angström exponent (AAE)* - and the chemical composition of ambient aerosol could open novel perspectives in real time source apportionment and air quality monitoring too (Sandradewi et al., 2008a, b; Lewis et al., 2008; Favez et al., 2009; Chakrabarty et al., 2010; Favez et al., 2010; Flowers et al., 2010; Ajtai et al., 2011; Moosmüller et al., 2011; Utry et al., 2014). Future studies should focus both on decreasing the integration time of toxicity tests and on defining the complex relationship between the physicochemical properties, the emitting sources and the toxicity of the fine and ultrafine PM fractions. Results of those could make significant contribution to planning more efficient air pollution strategies (de Kok et al., 2006).

Previous studies have shown that the optically active organic aerosol constituents (like Brown Carbon (BrC) including Humic Like Substances (HULIS)) can contribute to the toxicological potential of ambient aerosol (Donaldson et al., 1996; Donaldson et al., 2002; Li et al., 2003, 2009; Verma et al., 2009; Verma et al., 2012). In a recent study, Ács et al. (2013) found significant positive correlation between carbonaceous constituents of diesel exhaust like total carbon (TC) and polycyclic aromatic hydrocarbons (PAH). Turóczy et al. (2012) studied the ecotoxicological potential of airborne collected samples. Biomass burning emission was found to have an even higher ecotoxicological potential than particles from traffic emission. Recently, a large number of studies have demonstrated that optically active CPM constituents like BC and BrC can be selectively distinguished by their source specific spectral response (Favez et al., 2009; Ajtai et al., 2011; Utry et al., 2014; Ajtai et al., 2015).

Based on this, the aim of this study is to investigate the daily variation and the relationships between the on-line (physicochemical) and the off-line (toxicity and chemical composition) determined parameters to reveal the possibility of identifying of the ecotoxicological potential of ambient particulate matter through its real time measurable spectral response using state of the art instrumentation.

EXPERIMENTAL

Measurement Sites

The measurements were carried out during the winter of 2015 at two sites. Site 1 is a disused depot on the outskirts of the city of Szeged, Southern Hungary (46,284118°N, 20,170071°E). The campaign took place between 2015.01.07–2015.01.30. Site 2 is the observatory of the Hungarian Meteorological Service, in Budapest, the capital

of Hungary (47,430009°N, 19,181225°E). The measurements were carried out between 2015.02.09–2015.02.28. Both sites are located in suburban areas. We have previously shown that in Szeged - under wintry conditions - the two dominant sources of CPM are traffic and biomass burning (Utry *et al.*, 2014; Ajtai *et al.*, 2015). As opposed to Szeged, in case of Budapest, industrial activity is not negligible. There are several industrial areas in the surroundings of Site 2 as a result of which, presumably, traffic and biomass burning are not exclusive sources of CPM (Budapest környezeti állapotértékelése, 2014). The characteristic meteorological conditions of the two sites are summarized in Table 1.

Instrumentation and Sampling

The scope of the presented study is to determine the interdependences between the on-line and off-line measured parameters of ambient aerosol and co-emitted gaseous compounds. On-line measurements were carried out in-situ by the means of our previously developed mobile aerosol laboratory (Filep *et al.*, 2013; Utry *et al.*, 2014; Ajtai *et al.*, 2015). All applied instruments were connected to PM_{2.5} cut-off inlets during the campaign placed approximately 2 meters above the roof of the measurement platform.

Filter sampling was carried out with 6-hour time resolution by a Digital DHA-80 (Digital Elektronik GmbH) high volume aerosol sampler equipped with a PM_{2.5} cut-off inlet. Aerosol samples were collected on pre-treated Whatman QM-A Quartz Microfiber Filters (diameter of 150 mm) (GE Healthcare Life Sciences). Quartz filters were ignited at 680°C for 8 hours. Following that they were stored in aluminum film previously cleaned with acetone. Filter samples were analyzed off-line for chemical composition (Organic carbon (OC), Elemental carbon (EC), Total carbon (TC), Levoglucosan (LG), PAH concentrations) and ecotoxicity.

Online Measured Parameters

Optical absorption coefficient (OAC) was measured by our in-house developed multi-wavelength photoacoustic spectrometer (4λ-PAS). The photoacoustic method provides described in details elsewhere (Ajtai *et al.*, 2010a, b, 2011). The aerosol optical absorption coefficients (AOC) were determined at all operational wavelengths of the 4λ-PAS (266 nm, 355 nm, 532 nm and 1064 nm). Due to technical reasons, the optical absorption data at 266 nm were not available during this measurement campaign. The filter free operation and insensitivity to scattering. The wide range of operational wavelengths from the near-IR to the UV provides

absorption data with high reliability (Flowers *et al.*, 2010; Utry *et al.*, 2014). The principles of operation and the characteristic performance of the instrument are accuracy of the instrument was proved to be below 2–6% depending on the applied wavelengths due to the implemented wavelength independent gas-phase calibration (Ajtai *et al.*, 2010a, b).

Absorption Angström Exponent values were derived from the measured OAC data according to Eq. (1).

$$\frac{AOC(\lambda_1)}{AOC(\lambda_2)} = \left[\frac{\lambda_1}{\lambda_2} \right]^{-AAE} \quad (1)$$

where λ is the wavelength of irradiation, $AOC(\lambda)$ is optical absorption coefficient determined at the specific wavelength, and AAE is Absorption Angström Exponent.

Total number concentration (TNC) was determined by a Portable Aerosol Spectrometer (Model 1.109, Grimm Aerosol Technik GmbH & CO), measuring in the size range of 0.25–32 μm . Mass concentration (PM_{2.5}) was measured by a beta-ray attenuation spectrometer BAM-1020 (Met One Instruments Inc.). The concentration of gaseous species (CO, NO_x, and BTEX (benzene, toluene, m,p-xylen, o-xylen and ethylbenzene)) were determined by a Syntech Spectras GC955 Gas Chromatograph (Synspec b.v.).

Off-Line Analysis

Total carbon (TC) concentration was determined with a Zellweger Analytics Astro 2100 TOC Analyzer by the EGA method (hereafter quoted as (TC_{Zellweger})) from the filter collected samples. The carbon content of the sample was converted catalytically into CO₂ at 680°C and it was quantitated by an NDIR detector. Three replicates were measured from each sample. The levoglucosan (LG) concentration was determined as follows. First the filters were spiked with the internal standard methyl-beta-L-arabinopyranoside. The filters were dried and extracted in two steps. During the first extraction step dichloromethane was used, whereas in the second step the extractant was a 80:20 dichloromethane:methanol mixture. The extracts were filtered through a 0.45 μm syringe filter (Millipore Millex-HV). Following that the extracts were dried until dryness under a gentle stream of nitrogen. For derivatization a 50% BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) containing 1% of TMCS (trimethylchlorosilane) and 50% pyridine mixture was added to the samples and placed in an oven at 70°C for 3 h. The samples were measured with an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer. The separation was performed on an Agilent DB-5ms Ultra Inert capillary column (30 m \times 0.25 mm \times 0.25 μm).

EC, OC and TC (hereafter quoted as TC_{Sunset}) concentrations were determined by a thermo-optical Semi Continuous OCEC Analyzer (Sunset Laboratory Inc.) using protocol EUSAAR_2 (Cavalli *et al.*, 2010). EPA priority pollutants of 12 PAH compounds (phenantrene, anthracene, fluorantene, pyrene, Benzo[a]anthracene, chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, benzo[a]pyrene, Dibenz[a,h]anthracene,

Table 1. Characteristic meteorological conditions at the two measurement sites during the campaigns.

Site 1	Average	Min	Max
Temperature (°C)	4.14 \pm 2.68	–1.83	10.29
RH (%)	81.05 \pm 11.92	38.6	93.42
Wind speed (m s ^{–1})	1.15 \pm 0.84	0	4.09
Site 2	Average	Min	Max
Temperature (°C)	4.11 \pm 3.71	–5.14	11.77
RH (%)	70.99 \pm 16.73	20.53	92.67
Wind speed (m s ^{–1})	1.09 \pm 0.65	0	4.53

Benzo[g,h,i]perylene, Indenopyrene) were determined from filter extracts using High Performance Liquid Chromatography (HPLC). For the separation of PAHs, HPLC grade acetonitrile and water (from a MilliQ system, Water, Milford) were used. The LC system consisted of a Waters 600E pump, Rheodyne 7125 injector with 20 μ L loop, LiChrospher PAH column (250 \times 4 mm, dp = 5 mm) and Waters 470 fluorescence detector. Elution was provided by the following method: linear gradient from 40% acetonitrile in water to 100% acetonitrile in 20 min then 100% acetonitrile for 15 min at 1 mL min⁻¹. To achieve higher selectivity and sensitivity, time programmed excitation and emission wavelengths were used. Data acquisition and processing were provided by the Maxima 820 (Waters) chromatography software (Kiss et al., 2009).

Ecotoxicity (Vibrio Fischeri Bioluminescence Inhibition Bioassay)

For ecotoxicity testing, filter sample spots of 25 mm in diameter were cut then measured gravimetrically with a Sartorius microbalance (10 μ g sensitivity). These spots were ground in an agate mortar then transferred into pre-cleaned 4 ml vials with a PTFE-coated spatula. Suspensions were prepared adding 2 ml high-purity (MilliQ) water.

From the suspension, testing was carried out following the protocol as described in the ISO 21338:2010 standard. EC₅₀ and EC₂₀ values were calculated using Ascent Software provided by Aboatox Co., Finland. Ecotoxicity (EC₅₀) of a filter sample is determined as the absolute mass of particles that causes 50% reduction in the bioluminescence output of the test organisms relative to the control under the given experimental conditions. Therefore, EC₅₀ is expressed in units of μ g as calculated from measured mass of aerosol on the total filter by scaling to the area of the sample spot. The lower is the value of EC₅₀, the higher is the ecotoxicity of the sample.

RESULTS AND DISCUSSION

Statistical Summary and Daily Variations

Filter samples were collected with 6-hour time resolution. Filter sampling periods were 23:00–5:00, 5:00–11:00, 11:00–17:00 and 17:00–23:00. This way the different parts of the day could be differentiated as early morning, afternoon, evening and night and the daily variation of both the on-line and the off-line measured parameters determined. In order to compare these different diurnal periods, the on-line measured parameters were averaged over the same time interval of off-line filters. The statistical summary and the diurnal variation of all measured parameters can be found in case of Site 1 and Site 2 in Tables 2 and 3, respectively.

OACs, OC, EC, TCs, LG, AAEs, PM_{2.5}, PAH and BTEX concentrations showed characteristic but distinctive diurnal variations at the two sites. An increasing trend could be observed during the day at Site 1, however the above-mentioned parameters had diurnal variation with a daytime minimum during the day in case of Site 2.

CO was detected in the highest concentration during the night, whereas NO_x during the day. As CO mostly originates

from smoldering, it can be a tracer gas of biomass burning (Fine et al., 2002; Puxbaum et al., 2007). The diurnal variation of CO can carry information of the relative contribution of household heating to total PM (Koppmann et al., 2005). On the contrary, the highest NO_x concentrations were detected in the morning and in the early evening, when traffic activity is the highest (Sandradewi et al., 2008a, b; Favez et al., 2010; Utry et al., 2014).

Generally, in case of TNC no well-defined diurnal trend was observed. An exception is TNC, 0.25–0.5 μ m measured at Site 2. Based on these, in the next step, we examined the interdependences in between the measured parameter matrix (Tables 2 and 3).

Correlations between the Measured Parameters

Correlation analysis was carried out on the 6-hour averaged data in MATLAB by syntax “corrcoef” (www.mathworks.com). Pearson correlation coefficients (r) were determined in order to measure the linear association of two variables. Only correlations with a significance level (p-value) higher than 0.05 were considered.

Firstly, the correlations between the optical absorption coefficients determined at the specific wavelengths of our in-house developed multi-wavelength photoacoustic spectrometer (4 λ -PAS), the measured physicochemical aerosol parameters (organic, elemental, total carbon concentrations, levoglucosan concentration, number concentration, mass concentration and PAH concentration) and co-emitted gaseous species (NO_x, CO and BTEX) were investigated. Secondly, the relationship between ecotoxicity and the physicochemical parameters as well as co-emitted gaseous species was studied. Finally, correlation between the optical properties and ecotoxicity was analyzed. Pearson correlation coefficients (r) are listed in Tables 4 and 5. Unfortunately, due to technical reasons, the Sunset OCEC Analyzer was not available in case of Site 1. As a result of that the corresponding correlation coefficients are missing from Table 4.

Correlations between OACs and the Measured Physicochemical Parameters

Optical absorption coefficients show strong positive correlations (r > 0.6) with carbon and levoglucosan concentrations determined both by the Sunset OCEC Analyzer (OC, EC, TC_{Sunset}) and by analyzing filter extracts (TC_{Zellweg} and LG). This is in accordance with literature data, as optically active CPM has been shown to be the dominant in the fine particle size region (Braun et al., 2005; Shiraiwa et al., 2008; Bond et al., 2013). The wavelength dependency of the correlation strengths was also investigated. The strength of correlations shows wavelength dependency in case of Site 1, but not in case of Site 2. TC concentrations determined by the thermochemical (TC_{Sunset}) and the EGA method (TC_{Zellweg}) were in strong agreement (r = 0.967) at Site 2. As LG is a generally accepted marker of wood burning (Fine et al., 2002; Puxbaum et al., 2007), the very strong correlation (r = 0.953) between LG and OC indicates biomass burning to be the dominant contributor to OC concentrations at both sites.

Table 2. Statistical summary of measured raw data at the Site 1.

Site 1	23:00–05:00		05:00–11:00		11:00–17:00		17:00–23:00	
	(N = 21)		(N = 21)		(N = 20)		(N = 20)	
Measured parameter	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
OAC@1064nm [Mm ⁻¹]	1.95	0.74	3.55	1.4	4.06	1.52	4.54	2.1
OAC@532nm [Mm ⁻¹]	6.64	2.46	11.15	4.57	12.33	5.32	14.6	6.94
OAC@355nm [Mm ⁻¹]	22.56	10.17	34.63	17.31	37.58	16.98	47.62	23.72
AAE@1064–355nm	2.16	0.16	1.99	0.18	1.96	0.16	2.08	0.1
AAE@532–355nm	2.94	0.34	2.72	0.31	2.73	0.16	2.89	0.26
OC [μg m ⁻³]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EC [μg m ⁻³]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TC _{Sunset} [μg m ⁻³]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TC _{Zellweg} [μg m ⁻³]	10.63	4.93	14.3	7.67	14.89	7.35	18.97	9.62
LG [μg m ⁻³]	0.61	0.3	0.83	0.63	0.84	0.45	1.22	0.62
TNC, 0.25–0.5 μm [10 ⁶ counts l ⁻¹]	4.77	1.97	5.26	2.07	5.10	1.99	6.65	2.68
TNC, 0.5–1 μm [10 ⁶ counts l ⁻¹]	0.05	0.03	0.06	0.04	0.06	0.04	0.08	0.04
PM _{2.5} [μg m ⁻³]	31.81	15.08	28.27	11.8	26.96	11.73	31.19	13
Ecotoxicity (1/EC50) [μg ⁻¹]	0.21	0.16	0.11	0.15	0.06	0.07	0.23	0.41
Phenanthrene [ng m ⁻³]	1.55	1.06	1.97	1.6	2.51	1.7	3.22	3.85
Antracene [ng m ⁻³]	0.15	0.16	0.25	0.22	0.42	0.39	1.6	4.9
Fluorantene [ng m ⁻³]	2.64	1.58	4.42	2.21	7.15	5.1	7.23	4.83
Pyrene [ng m ⁻³]	4.58	2.79	8.3	4.95	12.41	10.24	12.09	7.3
Benzo[a]anthracene [ng m ⁻³]	1.42	0.84	3.72	2.96	4.61	2.87	7.3	5.44
Chrysene [ng m ⁻³]	2.67	2.01	5.07	3.79	5.79	3.58	8.78	6.26
Benzo[b]fluoranthene [ng m ⁻³]	2.7	1.68	4.83	3.19	5.43	3.13	7.69	4.31
Benzo[k]fluorantene [ng m ⁻³]	1.06	0.63	2.03	1.38	2.25	1.31	3.69	3.16
Benzo[a] pyrene [ng m ⁻³]	1.82	1.11	4.17	3.11	4.71	2.98	6.95	4.47
Dibenz[a,h] antarcene [ng m ⁻³]	0.31	0.23	0.67	0.66	0.71	0.55	1.65	3.35
Benzo[g,h,i]perylene [ng m ⁻³]	1.39	1.1	2.67	2.09	2.92	2.02	4.46	4.39
Indenopyrene [ng m ⁻³]	2.24	1.38	4.27	3.1	4.71	2.88	6.84	5
Benzene [ppb]	0.93	0.17	1	0.3	0.97	0.3	1.36	0.47
Toluene [ppb]	0.61	0.15	0.79	0.35	0.81	0.35	0.98	0.43
m,p-xylene [ppb]	0.31	0.08	0.51	0.22	0.59	0.38	0.64	0.32
o-xylene [ppb]	0.01	0.02	0.07	0.06	0.1	0.07	0.11	0.1
CO [ppm]	657	168	627	207	577	142	620	143
NO _x [ppb]	31.62	13.41	31.58	15.01	24.47	13.65	31.52	25.55

OAC values show moderate ($0.4 < r < 0.6$) and strong ($r > 0.6$) positive correlations with the TNC of particles with a mobility diameter between 0.25–0.5 μm. Interrelations become weaker with particles between 0.5–1 μm. These findings well agree with previous studies, where the count median diameter (CMD) of ambient light absorbing particles are the most dominant in the 0.25–0.5 μm size range (Braun *et al.*, 2005; Bond *et al.*, 2013). However, OAC shows moderate ($0.4 < r < 0.6$) correlation with PM_{2.5} mass concentration indicating that absorbing particles are mainly present in the fine size range (Shiraiwa *et al.*, 2008; Bond *et al.*, 2013).

OACs determined at the specific wavelengths show positive correlations with PAH concentrations determined from filter extracts and online measured BTEX, NO_x and CO concentrations in case of both sites.

Correlations between Ecotoxicity and the Measured Physicochemical Parameters

Ecotoxicity (EC50) shows correlations with parameters

indicating particle emission (Table 4) and parallel emitted gaseous constituents (Table 5). Ecotoxicity shows moderate correlations with TC_{Zellweg} and LG ($0.4 < r < 0.6$) at Site 1, while relationships are weaker ($0.2 < r < 0.4$) at Site 2. There are no OC, EC and TC_{Sunset} concentration data available at Site 1, however, in case of Site 2, weak relationships can be observed between carbon concentrations and ecotoxicity ($0.2 < r < 0.4$). Whereas there is weak and moderate relationship between ecotoxicity and PM_{2.5} mass concentration at Site1, no significant interdependence can be observed in case of Site 2. Ecotoxicity moderately correlates with NO_x and CO at Site 1, while relationships are weaker at Site 2. The same tendency can be observed in case of PAH compounds too. No significant correlation can be found between ecotoxicity and BTEX compounds. Although in this work we focused preliminarily on determining the toxicological potential of CPM selectively through its spectral response, we have to note that the *Vibrio fischeri* bioassay has also been recently found to be sensitive to the concentration of heavy and transition metals

Table 3. Statistical summary of measured raw data at the Site 2.

Site 2	23:00–05:00		05:00–11:00		11:00–17:00		17:00–23:00	
	(N = 30)		(N = 29)		(N = 29)		(N = 29)	
Measured parameter	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
OAC@1064nm [Mm^{-1}]	4.3	3.75	3.7	1.97	2.05	0.85	4.78	2.6
OAC@532nm [Mm^{-1}]	11.47	9.32	9.38	4.86	4.64	2.08	12.12	6.31
OAC@355nm [Mm^{-1}]	50.49	45.4	38.32	23.73	18.79	9.71	49.26	27.84
AAE@1064–355nm	2.22	0.13	2.1	0.27	2.02	0.25	2.13	0.23
AAE@532–355nm	3.83	0.47	3.47	0.47	3.45	0.71	3.63	0.65
OC [$\mu g m^{-3}$]	16.96	12.06	13.35	7.04	7.82	2.8	19.35	10.39
EC [$\mu g m^{-3}$]	1.96	1.4	1.97	0.91	1	0.4	2.73	1.22
TC _{Sunset} [$\mu g m^{-3}$]	18.91	13.42	15.32	7.8	8.82	3.09	22.07	11.51
TC _{Zellweg} [$\mu g m^{-3}$]	17.99	12.33	14.8	7.54	9.01	3.9	20.29	9.53
LG [$\mu g m^{-3}$]	1.26	1	0.79	0.49	0.35	0.16	1.4	0.85
TNC, 0.25–0.5 μm [10^6 counts l^{-1}]	0.93	0.59	0.8	0.41	0.49	0.25	0.89	0.53
TNC, 0.5–1 μm [10^6 counts l^{-1}]	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
PM _{2.5} [$\mu g m^{-3}$]	46.36	24.85	49.96	51.56	25.39	14.09	38.25	16.07
Ecotoxicity (1/EC50) [μg^{-1}]	0.13	0.09	0.06	0.07	0.02	0.04	0.15	0.13
Phenanthrene [$ng m^{-3}$]	4.41	3.81	3.24	1.57	1.61	0.73	4.87	3.24
Antracene [$ng m^{-3}$]	0.29	0.27	0.25	0.18	0.08	0.06	0.37	0.37
Fluorantene [$ng m^{-3}$]	7.42	7.31	5.91	3.68	2.78	1.23	10.18	8.07
Pyrene [$ng m^{-3}$]	19.25	21.18	12.33	8.61	4.85	2.51	28.6	24.12
Benzo[a]anthracene [$ng m^{-3}$]	6.13	7.98	3.46	2.44	0.84	0.58	10	8.4
Chrysene [$ng m^{-3}$]	6.89	7.44	4.59	3.29	1.28	0.67	10.11	8.33
Benzo[b]fluoranthene [$ng m^{-3}$]	6.29	5.72	4.38	2.45	1.5	0.77	8.52	6.01
Benzo[k]fluorantene [$ng m^{-3}$]	2.89	2.76	1.96	1.1	0.59	0.31	3.99	2.78
Benzo[a] pyrene [$ng m^{-3}$]	6.78	7.48	4.05	2.31	1.09	0.67	9.81	7.35
Dibenz[a,h] antarcene [$ng m^{-3}$]	0.6	0.55	0.41	0.31	0.12	0.09	0.84	0.88
Benzo[g,h,i]perylene [$ng m^{-3}$]	2.28	2.28	1.78	1.27	0.45	0.37	3.32	2.97
Indenopyrene [$ng m^{-3}$]	5.16	4.79	3.67	2.03	1.21	0.65	7.16	5.08
Benzene [ppb]	1.09	0.69	0.89	0.48	0.48	0.21	1.08	0.49
Toluene [ppb]	1.3	1.67	1.14	1.29	0.39	0.21	1.06	0.59
m,p-xylene [ppb]	0.73	0.75	0.76	0.64	0.26	0.21	0.83	0.51
o-xylene [ppb]	0.12	0.17	0.17	0.19	0.06	0.11	0.18	0.18
CO [ppm]	787	350	697	245	474	104	738	185
NO _x [ppb]	70.86	62.85	82.99	59.1	29.79	15.5	75.82	38.12

recently. Roig *et al.* (2013) found moderate correlations between the concentration of some of the transition and heavy metals in the PM samples. Therefore, considering the effect of the most dominant transition or heavy metals would further increase the relevancy of interpreting the correlations between the AAE and the toxicological potential of CPM.

Previous studies have shown that the carbonaceous fraction of PM has ecotoxicological potential (Túrocz *et al.*, 2012; Ács *et al.*, 2013). One specific aim of this study was to focus on the interdependences between the off-line studied toxicological potential and the online measured optical absorption response of CPM. Based on these, the fact that OACs also correlated with those parameters suggests that the ecotoxicity test could be sensitive to light absorbing carbonaceous particulate matter (LAC). In order to support this statement, in the following, we investigated the correlation between OACs and the result of the toxicity tests.

Relationship between Optical Absorption and Toxicity

In the previous section, we found a stronger correlation

between the measured chemical parameters linked to CPM and ecotoxicity (EC50) than with genotoxicity. In this section correlations between OACs and the results of the toxicity values are investigated (Table 6).

We found a positive relationship between ecotoxicity and OACs at both sites. At Site 1, weak to moderate correlations can be seen, where the strength of the relationship increases towards shorter wavelengths. At Site 2 the relationship is much weaker with no clear wavelength dependence. We suppose that, as opposed to Site 1, there are a third or more dominant sources of CPM present in case of Site 2 besides traffic and biomass burning (Budapest környezeti állapotértékelése, 2014; Utry *et al.*, 2014; Ajtai *et al.*, 2015) or the ecotoxicity is also affected by other constituents (i.e., metals) which don't contribute to absorption that can also worsen the correlations here.

The correlations and their wavelength dependence perceived at Site1 imply that there could be a relationship between AAE (being the wavelength dependency of optical absorption) and ecotoxicity too.

Table 4. Correlations between the measured parameters part 1.

Measured parameter		OAC@1064nm		OAC@532nm		OAC@355nm		Ecotoxicity (1/EC50)	
		Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
Sunset OCEC analyzer	Organic Carbon (OC)	n.a.	0.798	n.a.	0.807	n.a.	0.804	n.a.	0.245
	Elemental Carbon (EC)	n.a.	0.852	n.a.	0.866	n.a.	0.793	n.a.	0.267
	Total Carbon (TC _{Sunset})	n.a.	0.810	n.a.	0.818	n.a.	0.808	n.a.	0.250
Filter extraction	Total Carbon (TC _{Zellweg})	0.784	0.814	0.899	0.823	0.926	0.809	0.485	0.254
	Levoglucosan	0.759	0.780	0.825	0.809	0.869	0.785	0.502	0.266
Number size concentration	0.25–0.5 μm	0.734	0.567	0.815	0.747	0.824	0.760	0.487	0.290
	0.5–1 μm	0.449	0.475	0.406	0.574	0.371	0.579	0.268	0.228
Mass concentration	PM _{2.5}	0.544	0.449	0.681	0.434	0.653	0.420	0.561	-

Table 5. Correlations between the measured parameters part 2.

Measured parameters		OAC@1064nm		OAC@532nm		OAC@355nm		Ecotoxicity (1/EC50)	
		Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
NO _x		0.747	0.836	0.748	0.837	0.68	0.757	0.316	0.189
CO		0.754	0.788	0.807	0.827	0.833	0.792	0.393	0.3
PAH	Phenanthrene [ng m ⁻³]	0.479	0.825	0.653	0.811	0.639	0.798	0.276	0.193
	Antracene [ng m ⁻³]	0.382	0.607	0.514	0.597	0.504	0.537	-	0.194
	Fluorantene [ng m ⁻³]	0.57	0.795	0.698	0.786	0.669	0.728	0.318	0.186
	Pyrene [ng m ⁻³]	0.446	0.783	0.464	0.777	0.454	0.729	0.29	0.195
	Benzo[a]anthracene [ng m ⁻³]	0.687	0.775	0.744	0.777	0.744	0.725	0.364	0.212
	Chrysene [ng m ⁻³]	0.659	0.755	0.762	0.751	0.765	0.734	0.39	0.222
	Benzo[b]fluoranthene [ng m ⁻³]	0.731	0.771	0.829	0.778	0.835	0.744	0.425	0.246
	Benzo[k]fluorantene [ng m ⁻³]	0.691	0.799	0.804	0.808	0.805	0.775	0.346	0.247
	Benzo[a] pyrene [ng m ⁻³]	0.736	0.807	0.804	0.811	0.808	0.774	0.401	0.232
	Dibenz[a,h] antarcene [ng m ⁻³]	0.477	0.543	0.616	0.548	0.605	0.515	-	0.2
	Benzo[g,h,i]perylene [ng m ⁻³]	0.646	0.676	0.792	0.68	0.785	0.674	0.318	0.222
	Indenopyrene [ng m ⁻³]	0.709	0.773	0.835	0.779	0.832	0.748	0.371	0.242
	BTEX	Benzene	0.715	0.794	0.796	0.818	0.777	0.8	-
Toluene		0.672	0.651	0.718	0.658	0.686	0.643	-	-
m,p-xylene		0.571	0.788	0.588	0.796	0.53	0.714	-	-
o-xylene		0.623	0.644	0.651	0.673	0.557	0.548	-	-

Table 6. Relationship between OACs and toxicity.

	Ecotoxicity (1/EC50)	
	Site 1	Site 2
OAC@1064nm	0.335	0.23
OAC@532nm	0.384	0.275
OAC@355nm	0.424	0.22

Correlations coefficients determined between ecotoxicity, AAE and the levoglucosan to total carbon ratio (LG/TC_{Zellweg}) are demonstrated in Table 7. In case of Site1, ecotoxicity moderately correlates ($0.4 < r < 0.6$) with AAE@532–355nm. In case of AAE determined on a wider wavelength range, the relationship is weaker ($r = 0.309$). At Site 2 no significant correlation was found as expected from the findings in section 3.3.

Also, ecotoxicity shows moderate ($r = 0.486$) and weak ($r = 0.326$) correlations with the LG to TC ratio at both sites. As LG is a tracer of biomass burning (Fine *et al.*, 2002; Puxbaum *et al.*, 2007), LG/TC ratio can carry information regarding the relative strength of biomass burning compared

Table 7. Correlations between ecotoxicity, AAE and LG/TC ratio.

	Ecotoxicity (1/EC50)	
	Site 1	Site 2
AAE@1064–355nm	0.309	-
AAE@532–355nm	0.448	-
LG/TC _{Zellweg}	0.486	0.326

to other emitting sources. Site 1 has been previously shown to be dominated by biomass burning and traffic among urban wintry conditions. The relative strength of biomass burning to traffic can be indicated by LG/TC (Utry *et al.*, 2014; Ajtai *et al.*, 2015). The positive relationship between LG/TC and ecotoxicity verifies the findings by Túróczi *et al.* (2012) indicating that biomass burning emission has remarkable ecotoxicological potential.

In addition, we have previously demonstrated (Utry *et al.*, 2014; Ajtai *et al.*, 2015) that the daily variation of AAE can carry information regarding the relative strength of the two dominant LAC sources (traffic and wood burning),

thus the chemical composition of ambient aerosol particles (Sandradewi *et al.*, 2008a, b; Favez *et al.*, 2009; Ajtai *et al.*, 2015). Fig. 1 shows that the daily variations of the two quantities displayed similar trends during the campaign. It is worth to note that error bars related to any of the measured points do not indicate the uncertainty of the measured data but inherent attribute of presentation of daily variation in field measurement, where data is averaged according to the corresponding time periods and not the cohesive ambient factors such as meteorological or photochemical parameters (Sandradewi *et al.*, 2008a, b; Favez *et al.*, 2009). So, the correlation analysis is based on the averaged values which are representative for the diurnal variations. Consequently, the diurnal variation of the measured data is readable from this curve, even as a result of this primitive data evaluation method. However, the presented dataset is inadequate to disclose the way the realized correlations depend on ambient conditions. It is due to limited number of the measured data corresponding to the same time and coherent meteorological conditions. Fig. 1 only serves the purpose of displaying that the fluctuations in the daily variation AAE could serve as not only an indicator of the relative strength of the emitting sources of CPM but as a means for the preliminary assessment of the toxicological potential of CPM.

Although, the *Vibrio fischeri* bioassay only provides direct information regarding the toxicological effects of ambient aerosol on ecosystems, it has been proven appropriate to reveal spatial pattern of air pollution (e.g., Aammi *et al.*, 2017). To the authors best knowledge, we were the first to verify a correlation between the on-line measured optical response (OAC and AAE) determined by photoacoustic spectroscopy that is devoid of the methodological and analytical artifacts associated to the most commonly used optical absorption measurement techniques

(Collaud Coen *et al.*, 2010) and the offline determined toxicological potential of CPM. However, since previous studies have shown that the optically active organic fraction of ambient aerosol significantly contributes to the ecotoxicological potential of ambient particulate matter, we propose that there is a possibility for AAE to become an able candidate to obtain a first screening regarding the toxicological potential of optically active ambient CPM. In order to verify this proposition, longer measurement campaigns need to be carried out, where this proposition can be further confirmed in the function of both the different meteorological factors and the relative strength of emitting sources. Also, the effect of metals is not negligible, so simultaneous measurement of heavy and transition metal concentration in particulate matter would also be necessary to obtain a complex picture of the toxicological potential of CPM. In addition, as ecotoxicity determined by the *Vibrio fischeri* bioassay does not carry direct information on human health risks, so a possible correlation between the optical absorption properties of CPM and other toxicological assays should be investigated in the future.

SUMMARY AND OUTLOOK

An extensive 2-month field measurement campaign was carried out in order to investigate the relationship between the online measured optical, physicochemical and the offline determined chemical and the ecotoxicological properties of atmospheric particulate matter. The daily variation of the measured physicochemical and toxicological parameters was determined. The ecotoxicity test showed weak to moderate correlations with CPM emission, including the optical absorption coefficients determined at the specific operational wavelengths of the 4 λ -PAS. At Site 1 moderate

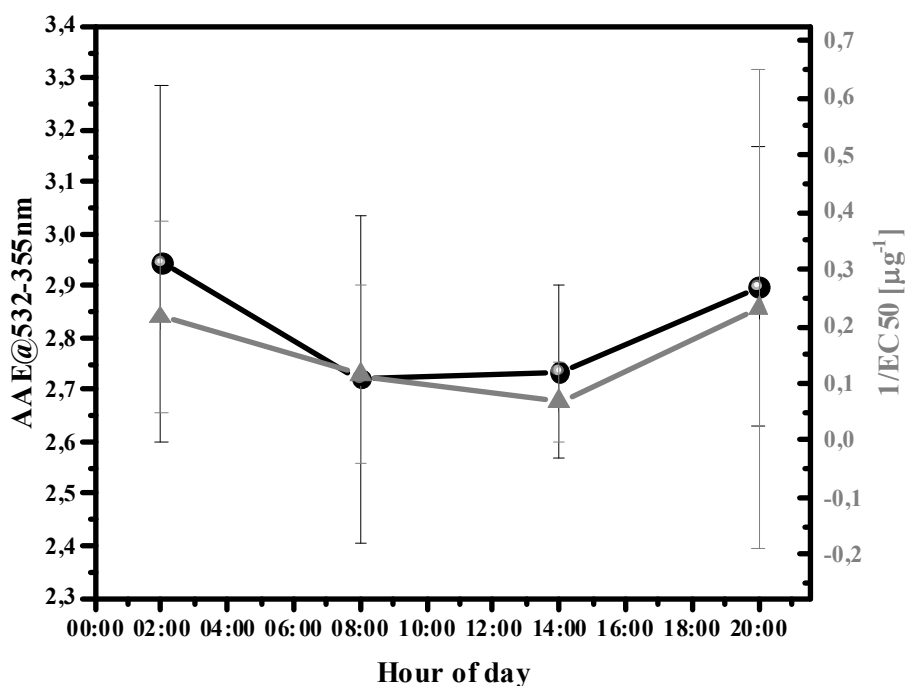


Fig. 1. The daily variation of AAE and ecotoxicity.

correlation was observed with the strength of the correlation increasing towards shorter wavelengths. At Site 2 the strength of the relationship was weaker, with no clear wavelength dependence. At Site 1 AAE@532–355nm showed moderate correlation with ecotoxicity.

This work should be considered as a preliminary study investigating the applicability of AAE as not only a chemically and source selective parameter but also a possible indicator of CPM toxicity. In this context, the realized weak or moderate correlations between ecotoxicity and AAE can be regarded as remarkable findings particularly if we consider the analytical and methodological difficulties associated with the toxicity measurements and the comparative interpretations of those, as well as the limitations of the applied data evaluation method (Kok *et al.*, 2005). Based on the determined correlations we propose that CPM has considerable ecotoxicological potential that could be prognosticated by real-time measured AAE values. However, in order to introduce an optical absorption measurement based real time air quality monitoring method, further long term studies have to be carried out including detailed analysis of the ambient effect of the correlation. Furthermore, the interdependence between the optical absorption spectrum of CPM and other toxicological indicators should be investigated in the future. Also, the toxicity of heavy and transition metals adsorbed on the surface of airborne particles should also be considered.

As stated by Kok *et al.* (2006) future research should also focus on investigating toxicity of fine and ultrafine ambient aerosol in relation to their emitting sources. We have recently demonstrated that the field application of multi-wavelength photoacoustic spectroscopy among wintry urban conditions can open up new possibilities in the real-time apportionment of the emitting sources of CPM (Utry *et al.*, 2014; Ajtai *et al.*, 2015). Based on the results of the present study and our recently developed multi-wavelength photoacoustic spectroscopy based real time apportionment method (Ajtai *et al.*, 2015) we are aiming to investigate ambient particulate matter toxicity in the function of emitting sources in the future. Also, the correlation between AAE and other toxicity tests should also be compared like oxidative potential assays, acellular methods or tests based on alveolar cells.

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