National Institute of Meteorology and Hydrology
Sofia, Bulgaria

The project "CARBOAEROSOL“ aims, objectives and some results"

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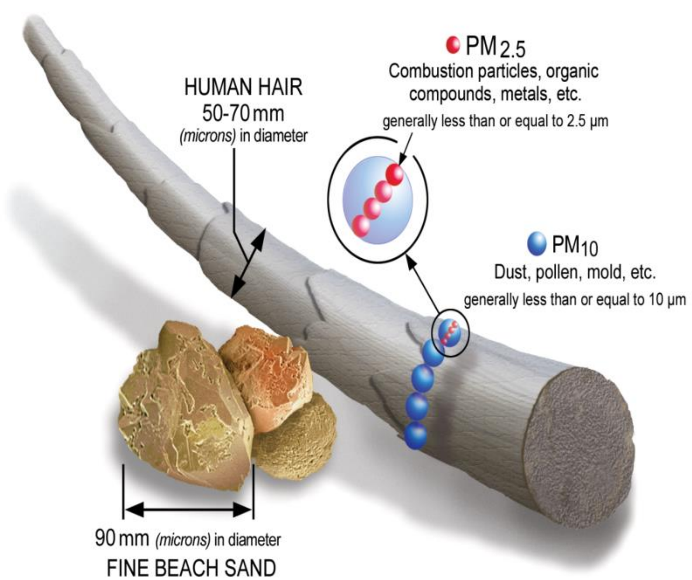
4th Scientific Seminar "Physics and chemistry of the Earth System" “,
village Banya, 9 -11 October 2022

Outline

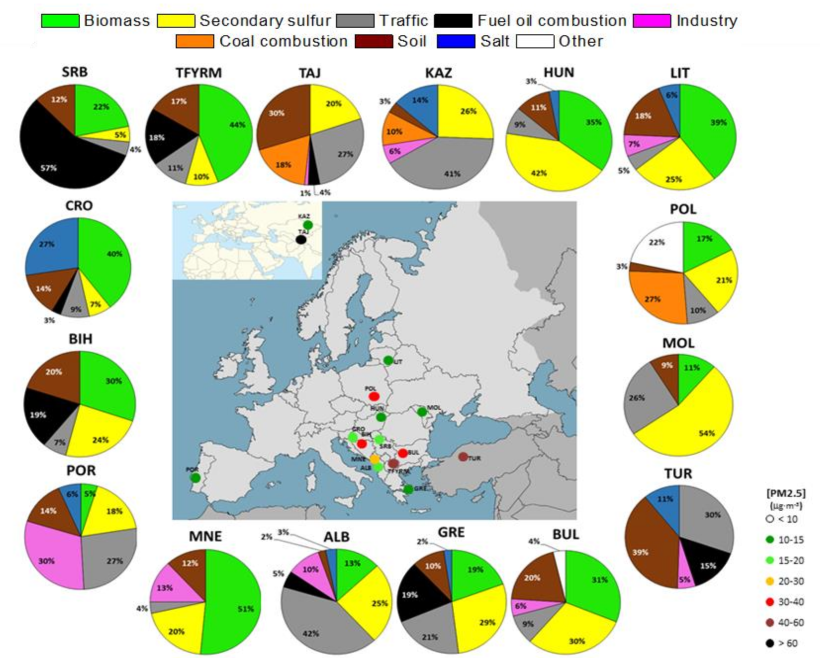
1. CARBOAEROSOL project - motivation and goals
2. Particulate matter bounded PAHs and Black carbon – *brief intro*
3. Sampling sites location, equipment and analysis
4. Some results
5. Work in progress

NIMH

- Fine particulate matter ($PM_{2.5}$) is a key air pollutant in terms of adverse health effects
- Many sources may contribute to $PM_{2.5}$ levels such as traffic, dust resuspension, biomass burning, industrial emissions, power plants, sea salt, ship emissions, etc.



https://www.epa.gov/pm-pollution/particulate-matter-pm-basics



S.M. Almeida et al. 2019

First study for Bulgaria (Sofia, PM10, 2012 – 2013)

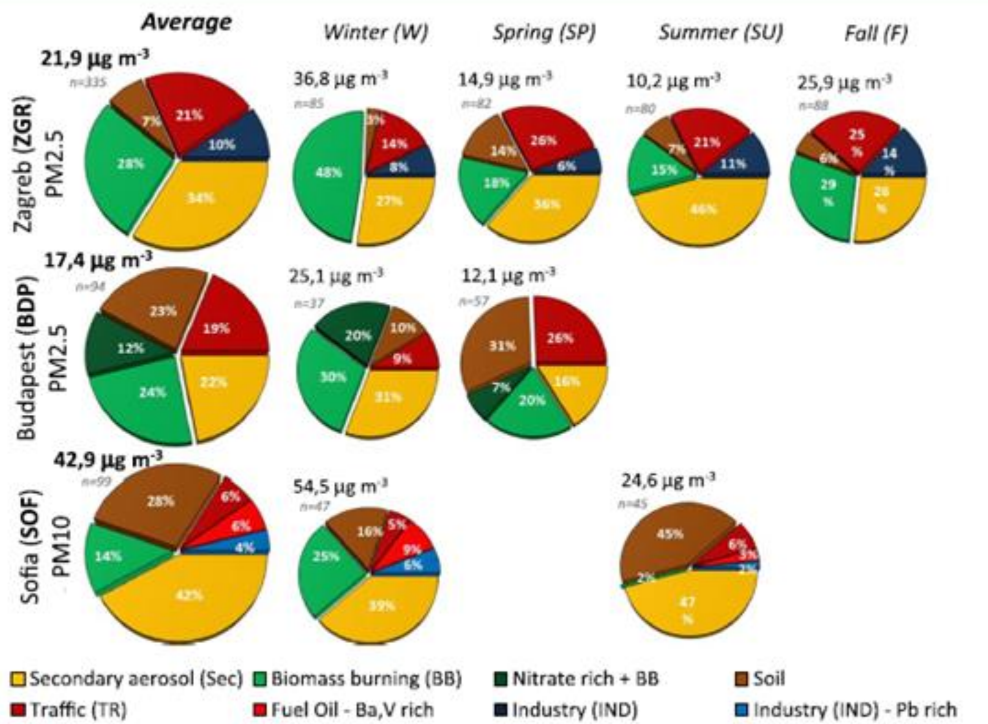
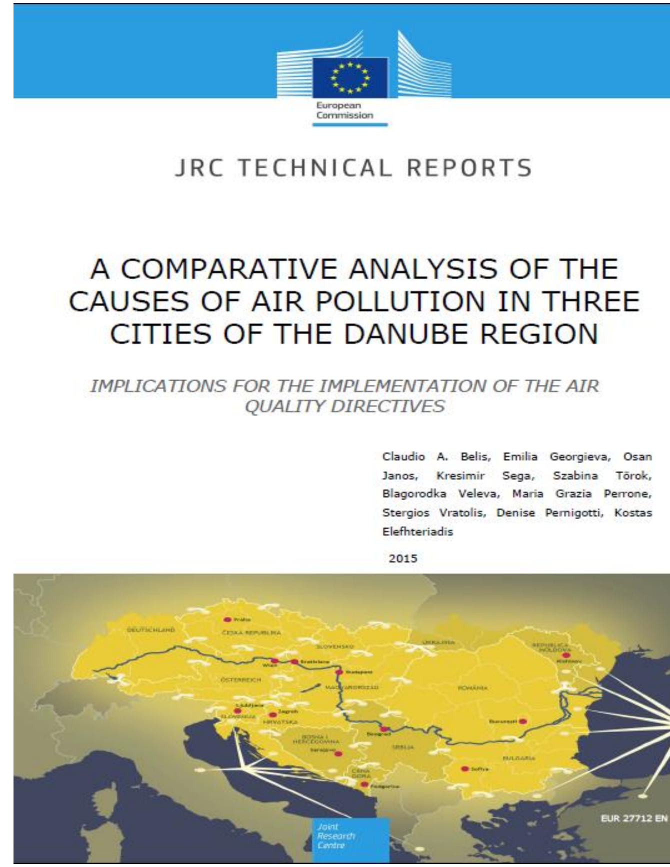


Fig. 5. Average and seasonal source contribution (cumulative percentage) to the PM by the PMF model in the three cities of the Danube macro-region.


European Commission

JRC TECHNICAL REPORTS

A COMPARATIVE ANALYSIS OF THE CAUSES OF AIR POLLUTION IN THREE CITIES OF THE DANUBE REGION

IMPLICATIONS FOR THE IMPLEMENTATION OF THE AIR QUALITY DIRECTIVES

Claudio A. Belis, Emilia Georgieva, Osan Janos, Kresimir Sega, Szabina Török, Blagorodka Veleva, Maria Grazia Perrone, Stergios Vratolis, Denise Pernigotti, Kostas Elefhteriadis

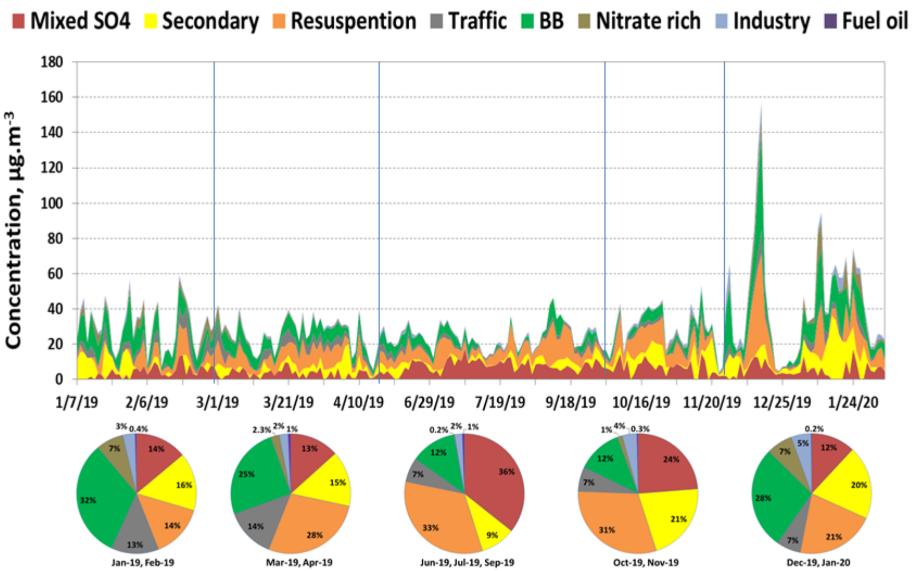
2015

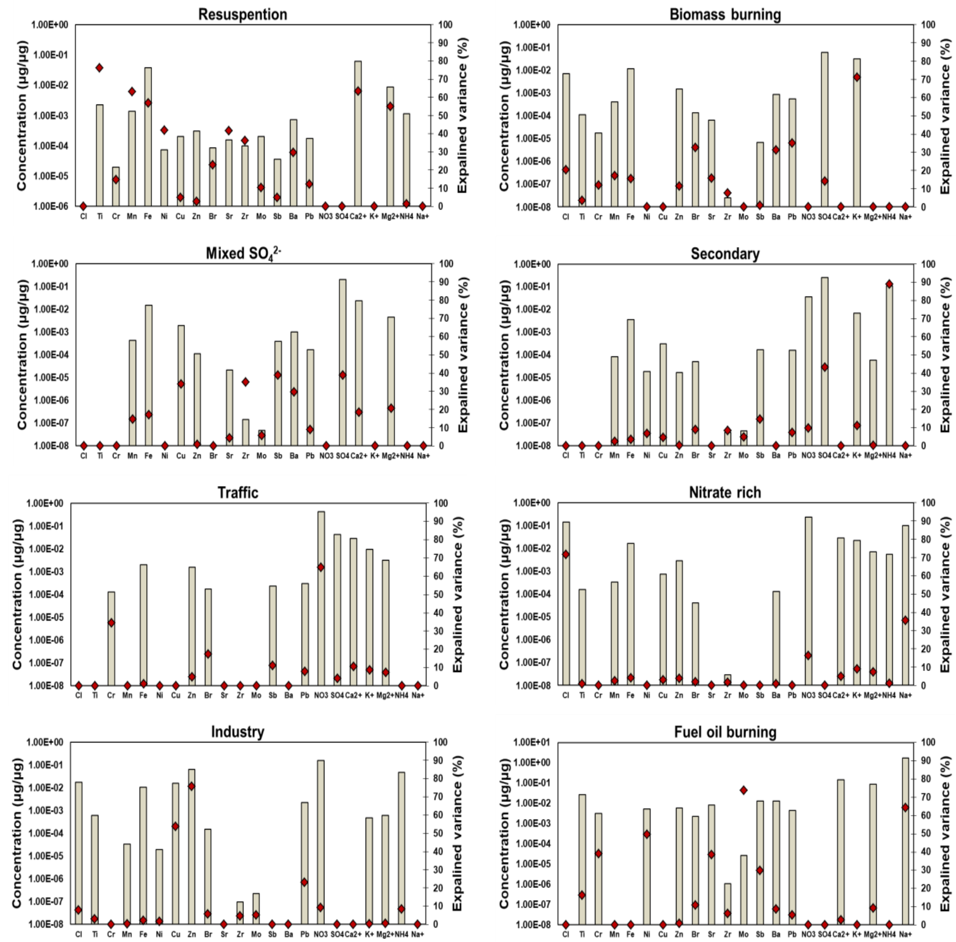
Joint Research Centre

EUR 27712 EN

M.G. Perrone, et. Al. , 2018

Source apportionment of PM10 in Sofia (2019 -2020)





33 elements by ED-XRF - Institute for Medical Research and Occupational Health, Zagreb

8 soluble ions – IC certified laboratory “Aquateratest” Sofia

No information for **Black carbon** and PAHs.

E. Hristova et. al. , 2020, Application of Positive Matrix Factorization Receptor Model for Source Identification of PM10 in the City of Sofia, Bulgaria. Atmosphere. 11(9):890. https://doi.org/10.3390/atmos11090890

CARBOAEROSOL

Study of black CARBOn and some important hydrocarbons in the atmospheric AEROSOL in an urban environment

ФНИ, № КП-06-Н 34/9 -19.12.2019

CARBOAEROSOL

Изследване на въглерод и някои значими въглеводороди в атмосферен аерозол в градска среда

Начало | Проект | Партньори | Дейности | Резултати | Контакти

НАЦИОНАЛЕН ИНСТИТУТ ПО МЕТЕОРОЛОГИЯ И ХИДРОЛОГИЯ 1890

УНИВЕРСИТЕТ "ПРОФ. Д-Р АСЕН ЗЛАТАРОВ" - БУРГАС

Колектив базова организация:

Доц. д-р Елена Христова – ръководител проект

Доц. д-р Благородка Велева
Доц. д-р Емилия Георгиева
Ас. Антон Петров
Математик Надя Нейкова
Физик Розета Нейкова

Колектив партньорска организация:

Гл. Ас.д-р Ления Гонсалвеш-Мусакова – ръководител колектив

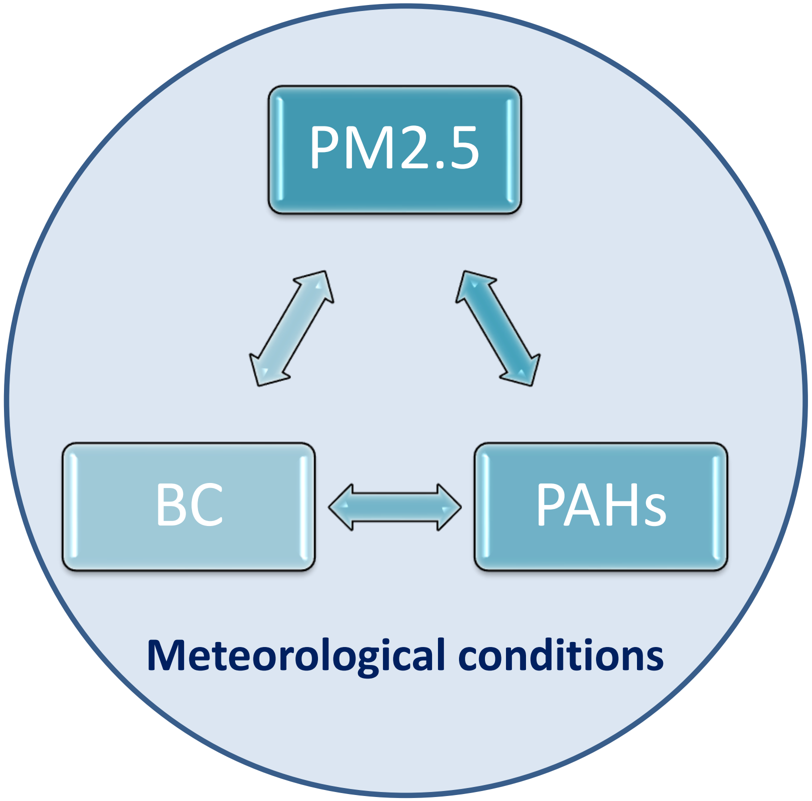
Ас. Стела Иванова Найденова
Проф. д-р Мая Дачкова Петрова-Стефанова
Химик д-р Зиля Адем Мустафа
Химик д-р Анифе Исмаил Вели

http://meteorology.meteo.bg/carboaerosol/index-bg.html

Five main work packages (WPs):

- ***WP1.*** *Organizing and conducting experimental field campaigns in Sofia and Burgas*
- ***WP2.*** *Determination of BC concentration in atmospheric aerosol (PM2.5)*
- ***WP3.*** *Determination of the PAHs concentration in PM2.5*
- ***WP4.*** *Investigation of the connections and correlations, between the meteorological parameters and the pollution levels with PM2.5, black carbon (BC) and PAHs for urban conditions in Bulgaria.*
- ***WP5.*** *Model results and comparative analysis*

WP/month	01-03	04-06	07-09	09-12	13-15	16-18	19-21	22-24	25-27	27-30	31-33	34-36
WP1	■	■	■	■	■	■	■					
WP2		■	■	■	■	■	■	■				
WP 3		■	■	■	■	■	■	■	■			
WP 4				■	■	■	■	■	■	■	■	■
WP 5		■	■	■	■	■	■	■	■	■	■	■

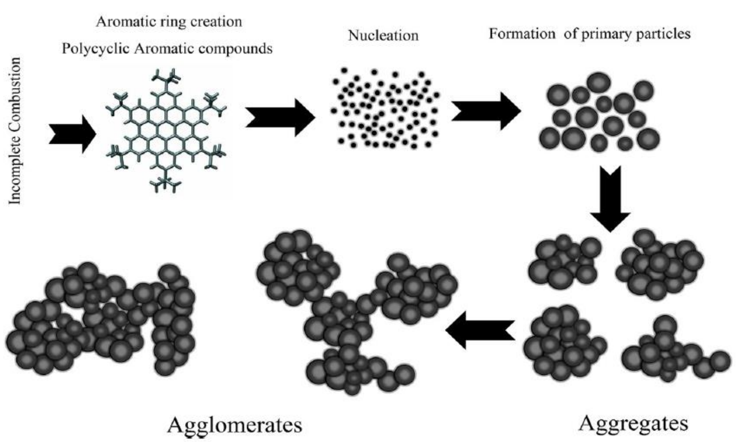


Motivation and Goal

Why BC and PAHs?

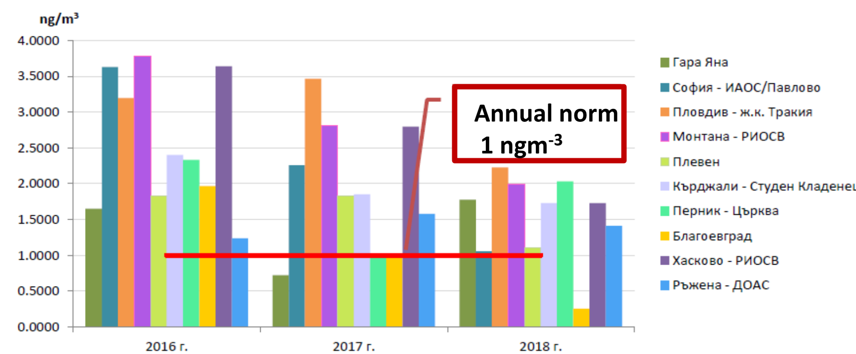
- A significant proportion of fine particle aerosol composition is comprised of black carbon (BC)
- Because of its harmful effect on the environment and human health
- The lack of information on the BC concentration in Bulgaria

- Mutagenic and carcinogenic nature
- Only benzo[a]pyrene (BaP) is determinate (10 stations in Bulgaria)
- Limited information on other priority PAH compounds



Source: M. U. Ali, 2020

Mean annual values of benzo(a)pyrene in Bulgaria

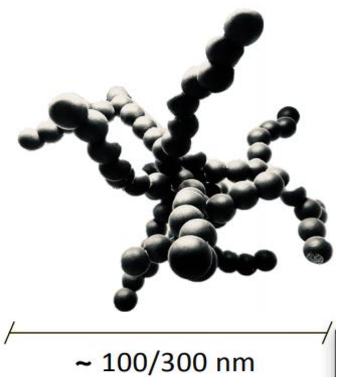


Source: ExEA

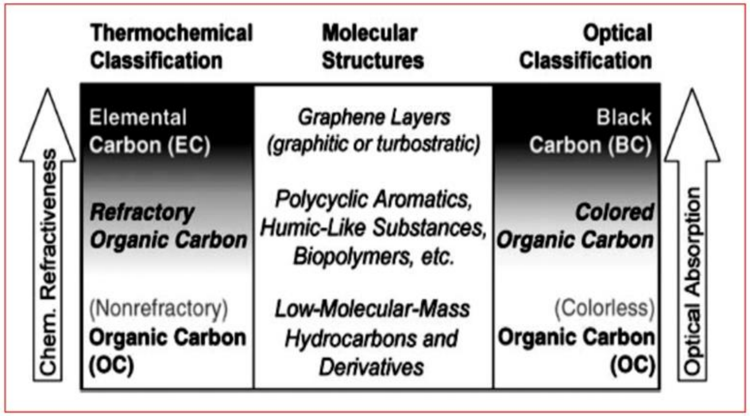
The aim – to study concentration of BC and PAHs bound to fine particulate matter $PM_{2.5}$ in two big cities in Bulgaria – Sofia and Burgas, based on parallel experimental campaigns.

What is a Black carbon?

- **SOURCES** - **carbonaceous aerosol formed through** incomplete combustion processes, mainly anthropogenic origins
- **Unique combination of the physical properties:**
  - strongly absorbs visible light
  - retains its basic shape at very high temperatures
  - insoluble in water, in organic solvents including methanol and acetone, and in other atmospheric aerosol components
  - exists as an aggregate of small carbon spheres
- **SIZE DISRIBUTION -** from 10 to 300 nm



Source: *Michele Bertò, ETH - NPC 2019*



Source: U. Poschl, AC, 2005

- **There is no universally accepted definition of the "black carbon"**

Optical methods - Light absorbing carbon **(LAC),** equivalent black carbon **(eBC)**

Thermochemical methods - Elemental Carbon **(EC)** and Organic Carbon **(OC)**

Polycyclic aromatic hydrocarbons (PAHs)

➢ Semivolatile organic compounds formed during the incomplete combustion and pyrolysis of organic material

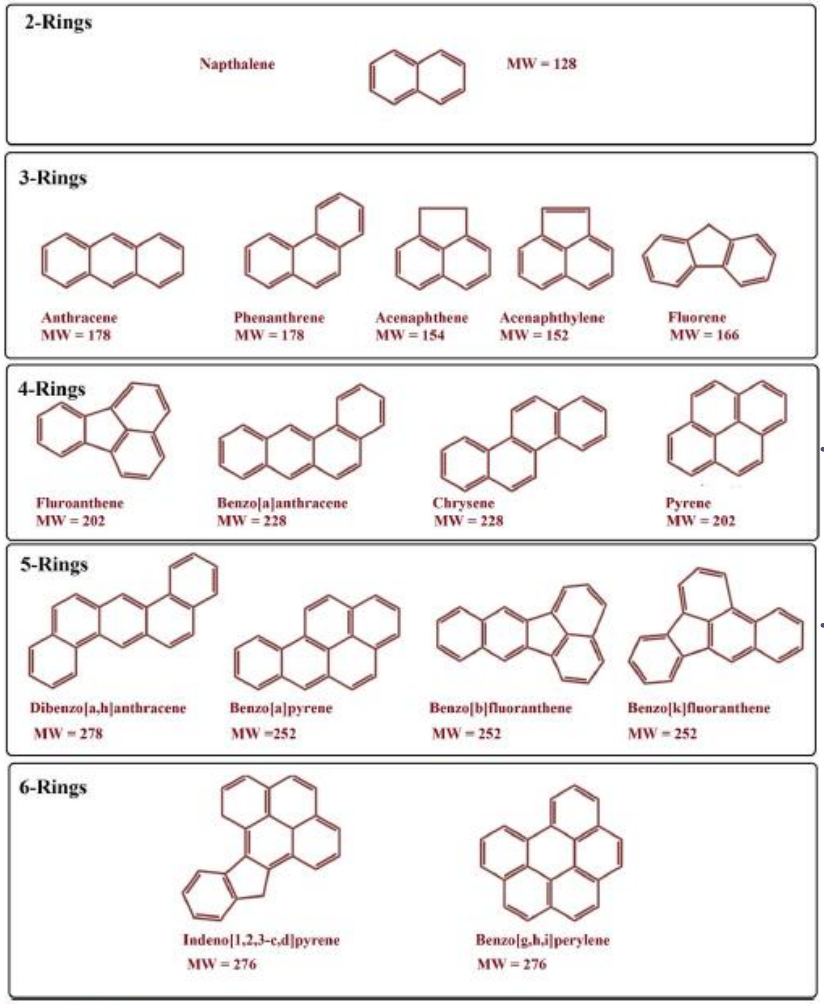


Figure 1. US EPA 16 priority polycyclic aromatic hydrocarbons structure and nomenclatures.

Generally divided into:

- Low-molecular-weight PAHs
  (LMW PAHs, *MW < 200 g/mol*)
- Medium-molecular-weight PAHs
  (MMW PAHs, *200 ≤ MW < 250 g/mol*),
- High-molecular-weight PAHs
  (HMW PAHs, *MW ≥ 250 g/mol*)

Sampling sites

Sofia

- 1.3 million inhabitants
- semi-closed Sofia valley
- surrounded by 4 mountains

Burgas

- 277 922 inhabitants
- Black Sea coast
- 4 large water bodies with different salinity

NIMH,
Central Meteorological Observatory,
(42.655 N, 23.384 E, at 586 m a.s.l.)

University "Prof. Dr Assen Zlatarov„
(42.3141N, 27.2647E, at 30 m a.s.l.)

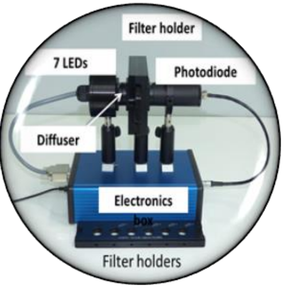
NIMH

Sampling equipment and analysis

Parallel $PM_{2.5}$ sampling

Teflon filters (47 mm PTFE, Whatman®)	**Quartz fiber filters** (47 mm, QMA, Whatman®)

Determination of $PM_{2.5}$ mass concentrations



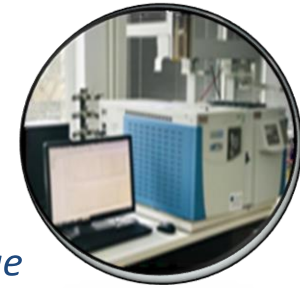
Estimation of BC and BrC

Multi-wavelength Absorption Black Instrument (MABI)

405nm, 465nm, 525nm, 639nm, 870nm, 940nm, 1050nm

Sample preparation

- *Spiked filters with recovery standards*
- *Ultrasonicated extraction*
- *Extracts purification and concentration*



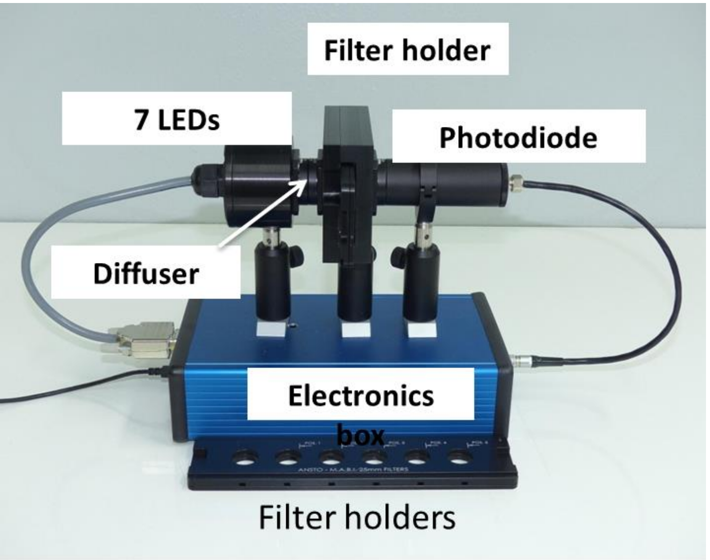
PAHs analyses

-GC–MS/MS, Thermo Scientific Trace 1300/TSQ 8000 in the selected reaction monitoring (SRM)

- *Internal standard calibration technique*

Estimation of BC in $PM_{2.5}$

- Multi-wavelength Absorption Black instrument (**MABI**) developed at Australian Nuclear Science and Technology Organisation
- This instrument measures light absorption (*I_o and I*) at seven different wavelengths, spanning ultraviolet to infrared (**405nm, 465nm, 525nm, 639nm, 870nm, 940nm and 1050nm**)
- Possibilities to differentiate the contributions from sources such as biomass burning (BC_{bb} or BrC) and motor vehicles-traffic (BC or BCff).



Atanacio A. J., Cohen D. D., Button D., Paneras N., Garton D., 2018, Multi-wavelength Absorption Black Carbon Instrument (MABI) Manual

- Three steps for calculation:

Determination of black carbon light absorption coefficient

$$b_{abs} = 10^2 \left[\frac{A}{V}\right] ln \left[\frac{I_o}{I}\right]$$

A - filter collection area in cm^2
V - volume of air sampled through the filter in m^3
I_o - measured light transmission through blank filter
I - measured light transmission through exposed filter

Mass absorption coefficient (ε):

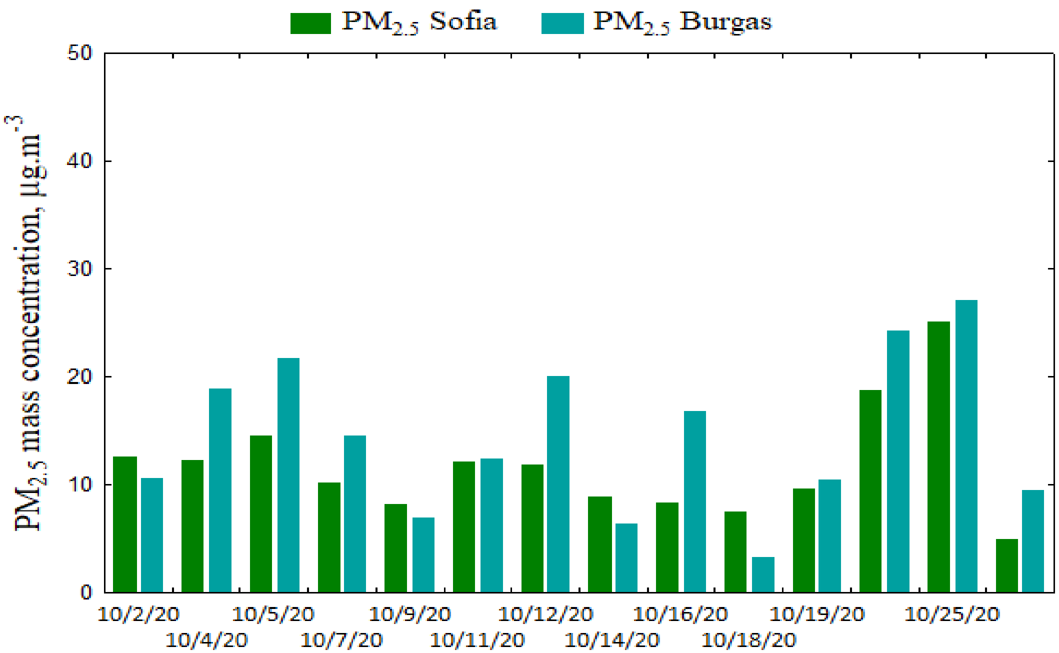
$$\varepsilon = a\lambda^b$$

Light absorbing carbon (LAC) concentration

$$LAC(ngm^{-3}) = \frac{10^5[A(cm^2)]}{[\varepsilon(m^2g^{-1})][V(m^3)]} ln \left[\frac{I_0}{I}\right]$$

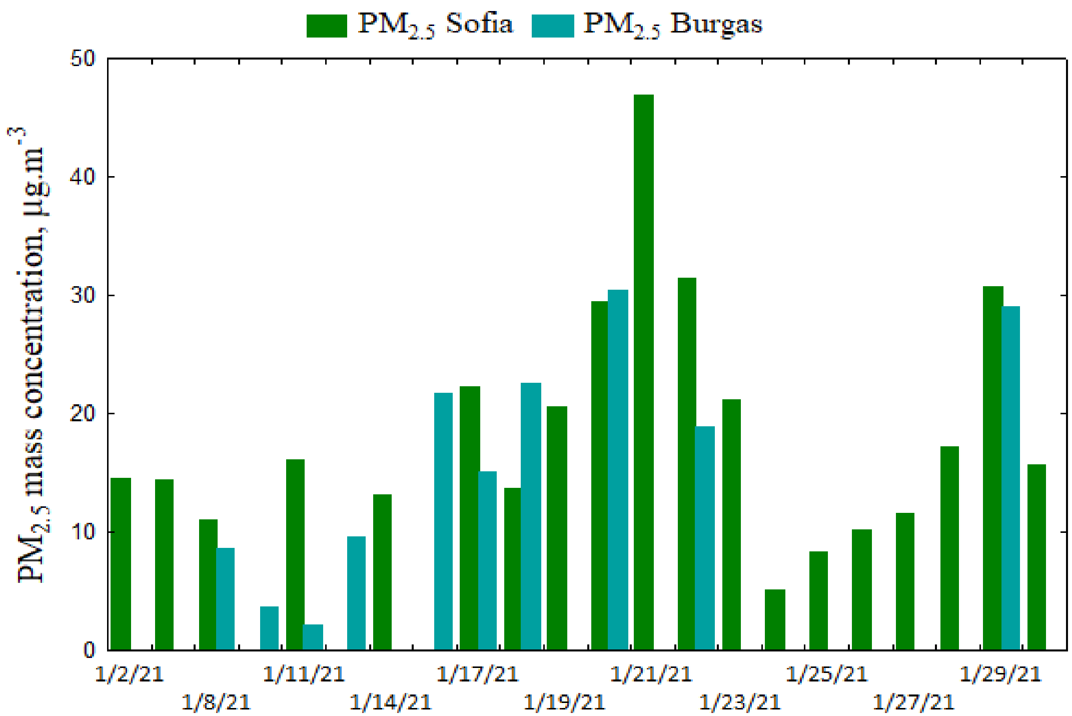
- ***BC** = LAC ($\lambda_{639\ nm}$)*
- ***BrC** = LAC (λ_{405nm}) – LAC (λ_{1050nm})*

Some results



October 2020

January 2021



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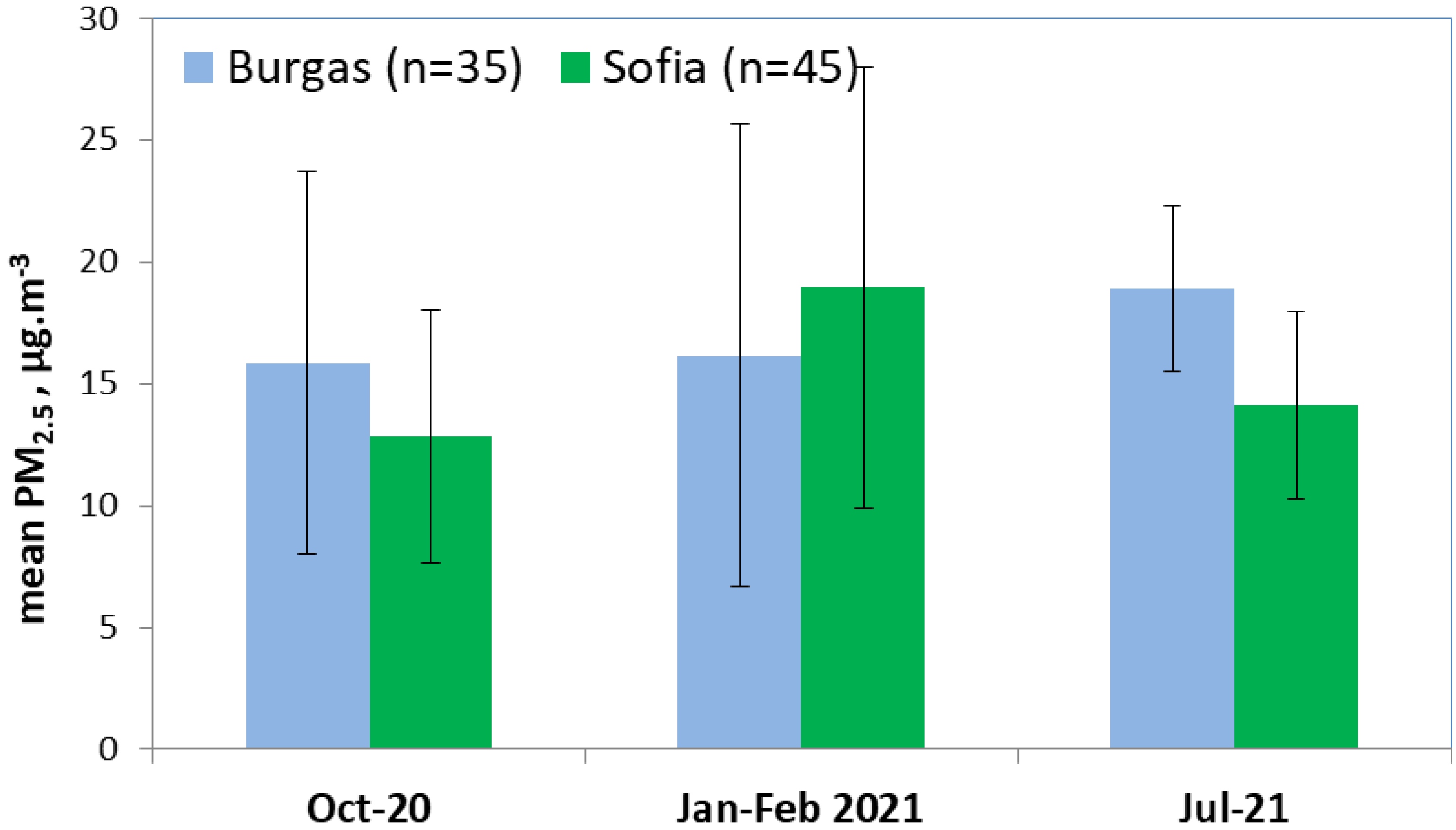
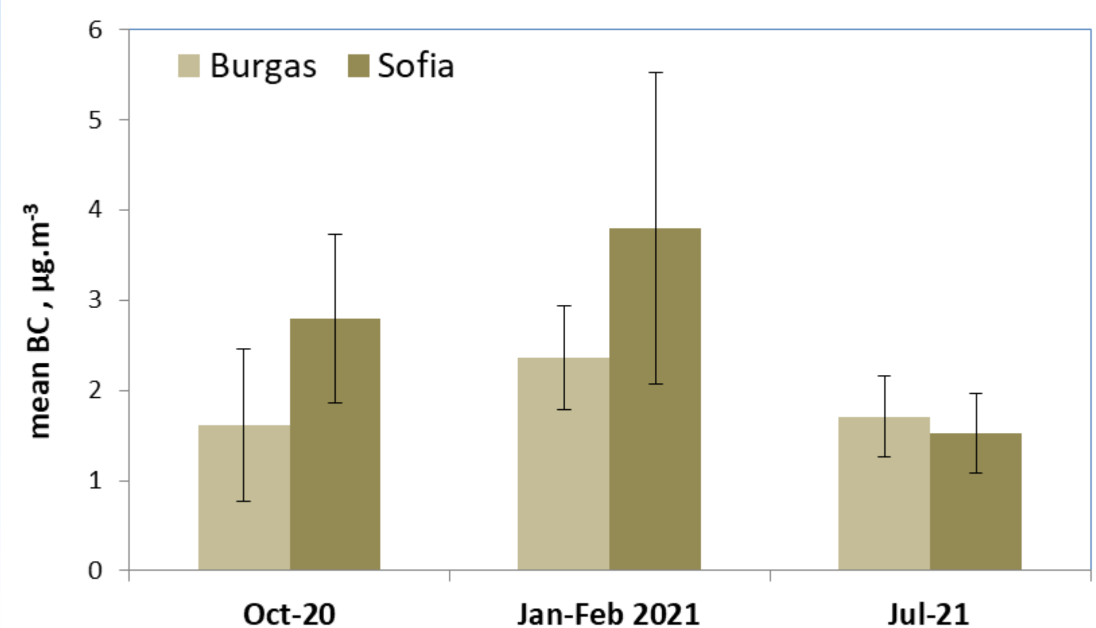


Burgas (n=35)
Sofia (n=45)
mean $PM_{2.5}$, $\mu g.m^{-3}$
30
25
20
15
10
5
0
Oct-20
Jan-Feb 2021
Jul-21

NIMH

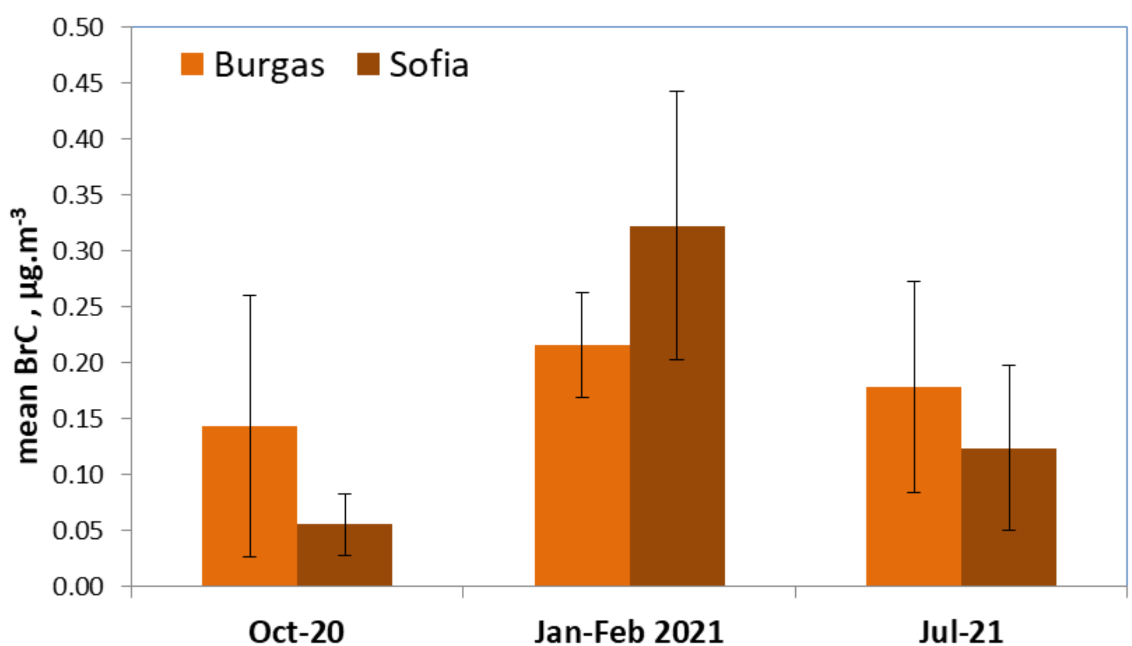


$BC/PM_{2.5}$

	Oct	Jan-Feb	Jul
Burgas	10%	15%	9%
Sofia	22%	20%	11%

$BrC/PM_{2.5}$

	Oct	Jan-Feb	Jul
Burgas	0.9%	1.3%	0.9%
Sofia	0.4%	1.7%	0.9%



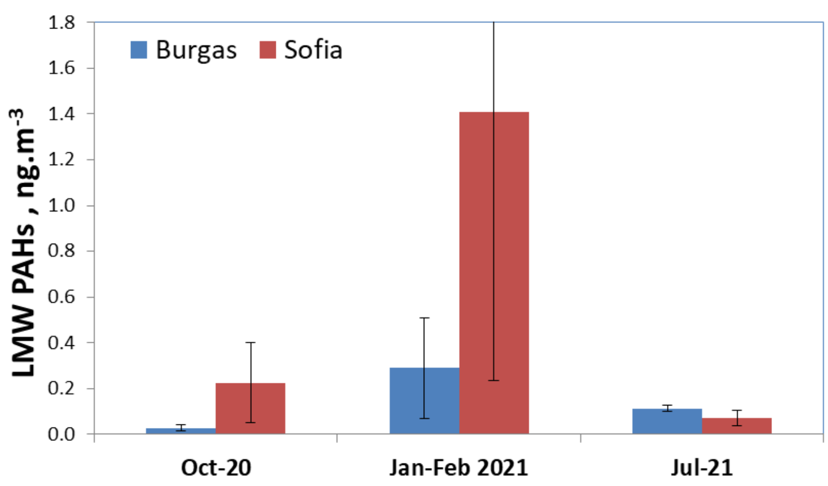
Correlation matrixes for $PM_{2.5}$, BC, BrC, NO_2, CO and meteorological parameters (T- temperature, PR – precipitation rate, RH – relative humidity, WS – wind speed) for January 2021

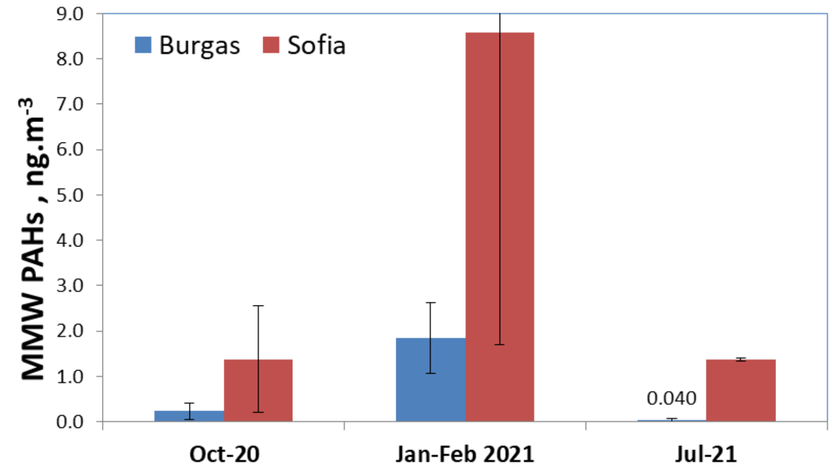
Sofia	BC	BrC	$PM_{2.5}$	CO	NO_2	T	PR	RH	WS
BC	1.00								
BrC	-0.15	1.00							
$PM_{2.5}$	**0.94***	-0.21	1.00						
CO	**0.85**	**-0.59**	**0.82**	1.00					
NO_2	**0.87**	-0.45	**0.83**	**0.86**	1.00				
T	0.18	-0.02	-0.06	0.22	0.31	1.00			
PR	-0.49	-0.35	-0.17	-0.07	-0.19	-0.45	1.00		
RH	-0.13	**-0.61**	-0.02	-0.08	-0.03	-0.36	**0.72**	1.00	
WS	**-0.80**	0.28	**-0.73**	**-0.57**	**-0.82**	-0.35	0.30	0.08	1.00

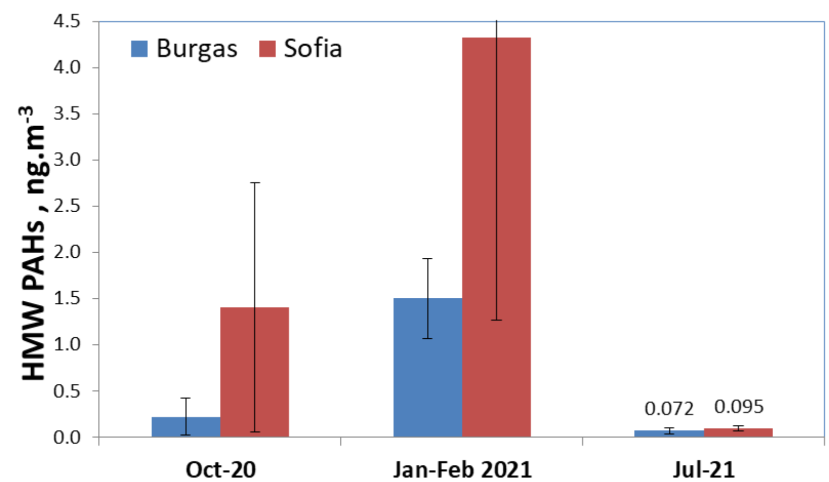
Burgas	BC	BrC	$PM_{2.5}$	CO	NO_2	T	PR	RH	WS
BC	1.00								
BrC	-0.07	1.00							
$PM_{2.5}$	**0.95**	-0.13	1.00						
CO	**0.84**	0.15	**0.81**	1.00					
NO_2	**0.74**	-0.37	**0.79**	**0.81**	1.00				
T	-0.51	-0.48	-0.58	-0.43	-0.14	1.00			
PR	**-0.75**	0.61	**-0.73**	-0.54	**-0.76**	0.62	1.00		
RH	**-0.64**	-0.46	**-0.66**	-0.56	-0.27	**0.86**	**0.79**	1.00	
WS	**-0.76**	-0.20	**-0.77**	**-0.84**	-0.62	0.58	0.53	**0.83**	1.00

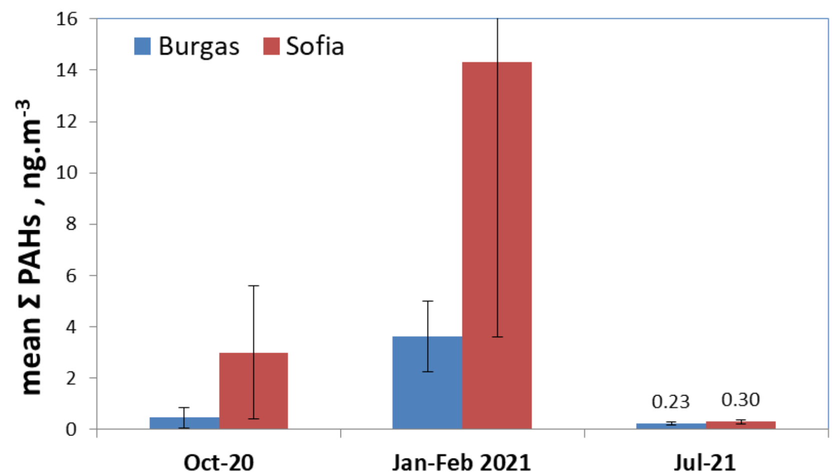
*Statistically significant correlation coefficients ($p < 0.05$) are bolded, *NO_2 and CO data is from ExEA*

NIMH


Burgas
Sofia
LMW PAHs , ng.m-3
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Oct-20
Jan-Feb 2021
Jul-21


Burgas
Sofia
MMW PAHs , ng.m-3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.040
Oct-20
Jan-Feb 2021
Jul-21


Burgas
Sofia
HMW PAHs , ng.m-3
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.072
0.095
Oct-20
Jan-Feb 2021
Jul-21


Burgas
Sofia
mean Σ PAHs , ng.m-3
16
14
12
10
8
6
4
2
0
0.23
0.30
Oct-20
Jan-Feb 2021
Jul-21

NIMH

Estimation of cancer risk of **PAHs**

- All PAH compounds have carcinogenic and mutagenic potencies, but *BaP* is considered as the strongest one and is often used as an indicator of human exposure to PAHs.
- For estimation of the toxic equivalency (TEQ) of the total PAH concentration, the carcinogenic potencies of individual PAHs are expressed relative to the potency of BaP, as the concentration of each individual PAH compound is multiplied by a specific toxic equivalency factor (TEF)

$$\text{TEQ}\ \Sigma\ \text{PAHs} = \sum_{i}^{n=1} BaP_{TEQ} = \sum_{i}^{n=1} C_i x TEF_i$$

C_i is the concentration of the i^{th} target compound (ng m^{-3})

- Additionally, excess cancer risk from inhalation (ECR) can be calculated using

$$ECR = TEQxUR_{BaP}$$

UR_{BaP} is the inhalation cancer unit risk factor of *BaP*

This is defined as the number of people at risk of contracting cancer from inhalation a *BaP* equivalent concentration of 1ng m^{-3} within their lifetime of 70 years. The World Health Organization (WHO) value of UR_{BaP} is 8.7×10^{-5}

Toxic equivalency of BaP_{TEQ}

Sofia	Oct-20			Jan-Feb 21			Jul-21		
	TEQ Σ PAHs	Σ PAHs		TEQ Σ PAHs	Σ PAHs		TEQ Σ PAHs	Σ PAHs	
	ng m^{-3}	ng m^{-3}	%*	ng m^{-3}	ng m^{-3}	%*	ng m^{-3}	ng m^{-3}	%*
Average	0.39	3.60	0.027	1.85	15.31	0.078	0.04	0.38	0.003
SD	0.43	3.01	0.015	1.41	11.63	0.037	0.01	0.08	0.001
Min	0.02	0.76	0.006	0.24	1.87	0.031	0.01	0.28	0.002
Max	1.52	11.33	0.054	5.28	38.47	0.148	0.06	0.53	0.004

** Σ PAHs като част от $ФПЧ_{2,5}$, %*

Burgas	Oct-20			Jan-Feb 21			Jul-21		
	TEQ Σ PAHs	Σ PAHs		TEQ Σ PAHs	Σ PAHs		TEQ Σ PAHs	Σ PAHs	
	ng m^{-3}	ng m^{-3}	%*	ng m^{-3}	ng m^{-3}	%*	ng m^{-3}	ng m^{-3}	%*
Average	0.04	0.83	0.008	0.53	4.08	0.017	0.03	0.31	0.002
SD	0.05	0.46	0.008	0.18	1.71	0.009	0.01	0.10	0.000
Min	0.00	0.36	0.002	0.32	2.44	0.008	0.00	0.15	0.001
Max	0.18	2.00	0.027	0.75	6.42	0.029	0.05	0.45	0.002

** Σ PAHs като част от $ФПЧ_{2,5}$, %*

Excess cancer risk from inhalation of PAHs

	Oct	Jan-Feb	Jul	Mean
Burgas	3.51E-06	4.56E-05	2.62E-06	3.04E-06
Sofia	3.36E-05	1.60E-04	3.10E-06	7.18E-05

The estimate of cancer risk from PAHs expressed by ECR shows a lower value compared to the acceptable limit (≥10^{-3}), even during the cold period of the study, and should not be considered as serious with a high priority to address.

Diagnostic ration for source identification of PAHs in $PM_{2.5}$

Diagnostic Ratio	Indicator Source		Burgas			Sofia		
			Oct-20	Jan-Feb 21	Jul-21	Oct-20	Jan-Feb 21	Jul-21
BaP/BghiP	<0.6	traffic	0.47	1.14	2.93	0.81	1.77	2.66
	0.9-6.6	coal combustion						
BaA/(BaA+Chr)	<0.2	unburned petroleum (petrogenic)	0.46	0.30	0.11	0.37	0.36	0.21
	>0.35	pyrogenic						
	0.2-0.35	mixture of both						
BaP/(BaP+Chr)	<0.5	diesel vehicles	0.29	0.36	0.42	0.34	0.36	0.42
	>0.5	gasoline vehicles						
Fla/(Fla+Pyr)	0.4-0.5	petroleum (liquid fossil fuel) combustion	0.31	0.47	0.45	0.36	0.43	0.46
	>0.5	grass/wood/coal combustion						
	0.42-0.53	road dust						
IndP/(IndP+BghiP)	<0.2	unburned petroleum (petrogenic)	0.49	0.59	0.78	0.52	0.65	0.71
	0.2-0.5	petroleum (liquid fossil fuel) combustion						
IndP/BghiP	>0.5	grass/wood/coal combustion	0.98	1.45	2.79	1.08	1.86	2.57
	0.35-0.7	diesel vehicles						
	<0.4	gasoline vehicles						
	≈1	diesel vehicles						

Work in progress

- Parallel sampling of PM2.5 in Sofia and Burgas continues
- Analysis of BC and PAHs
- Information on meteorological elements
- Testing the applicability of the EPA PMF 5.0 receptor-oriented model system with the obtained BC and PAH data
- Dissemination of the obtained results
- Organisation of a workshop at the end of the project

_С П И С Ъ К_

на научните публикации по проект

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Thank you for your attention!

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