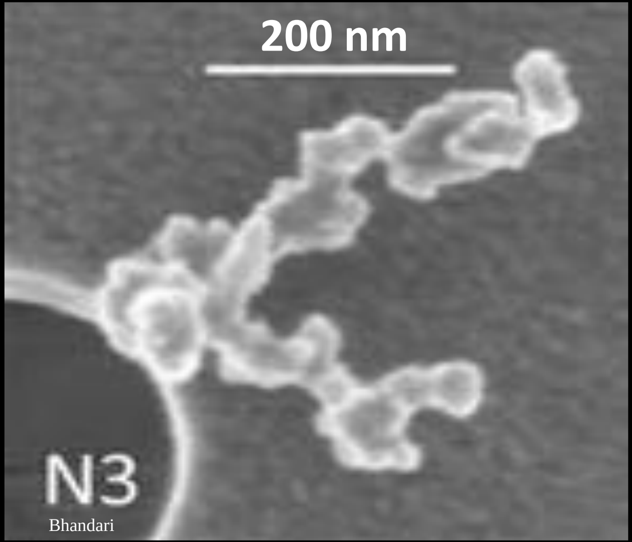
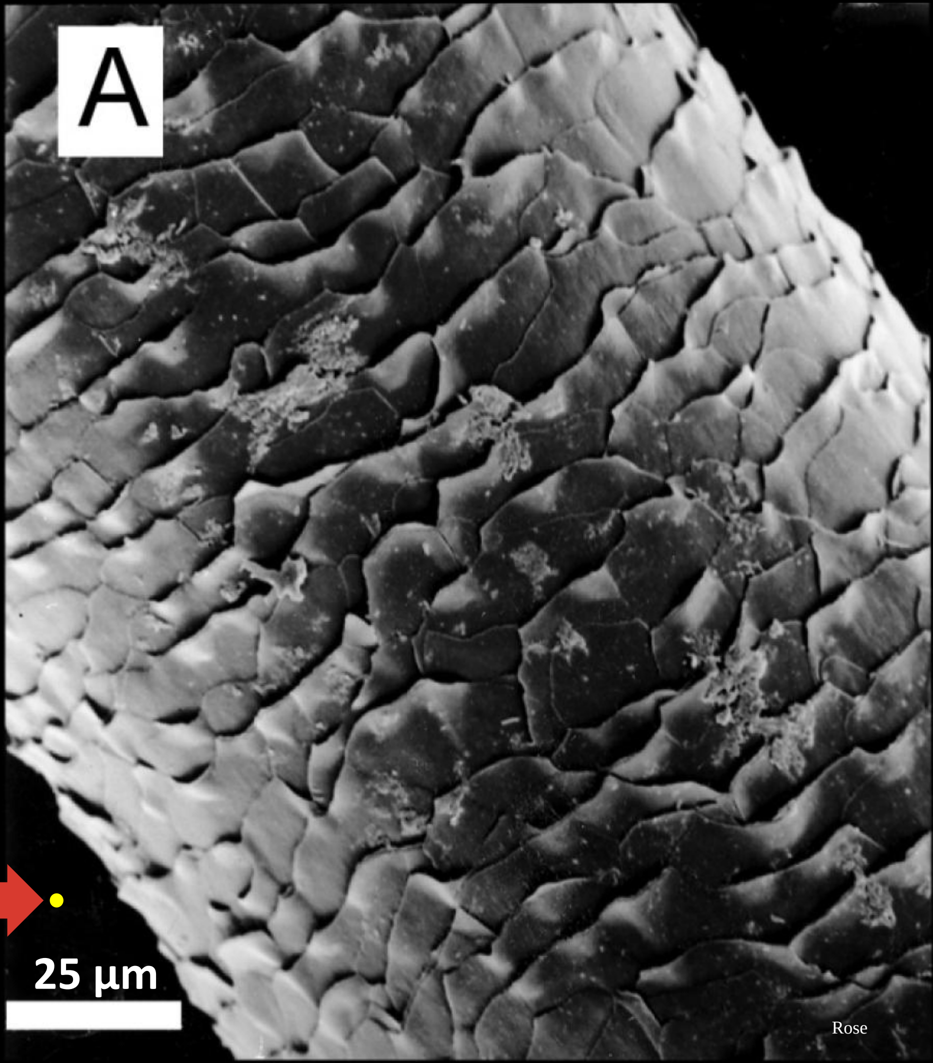
Standardizacija črnega ogljika in meritve oksidacijskega potenciala

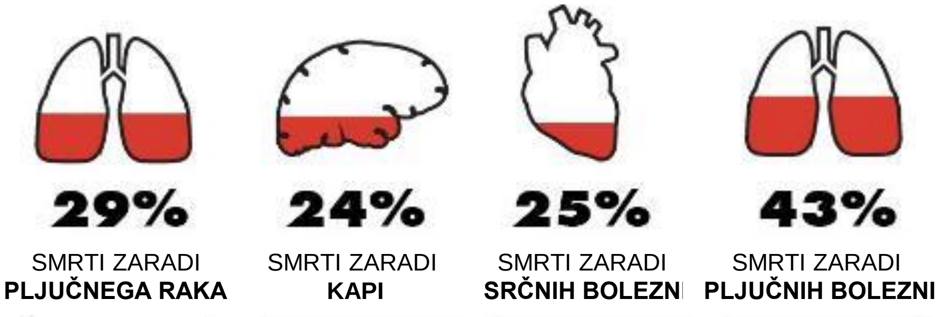
Griša Močnik, U. Jagodič, L. Pirker, M. Škarabot, M. Kurtjak, K. Vidović, L. Ferrero, B. Visser, J. Röhrbein, E. Weingartner, D.M. Kalbermatter, K. Vasilatou, T. Bühlmann, C. Pascale, T. Müller, A. Wiedensohler, D. Bell, R. Modini, M. Gysel Beer, A. Prevot, L. Drinovec

K. Glojek, V. Dinh Ngoc Thuy, S. Weber, G. Uzu, M. Manousakas, R. Elazzouzi, K. Džepina, S. Darfeuil, P. Ginot, J.–L. Jaffrezo, R. Žabkar, J. Turšič, A. Podkoritnik and **G. Močnik**


200 nm
N3
Bhandari


A
25 µm
Rose

Onesnažen zrak:
največja okoljska grožnja zdravju



Največji negativni učinki zaradi delcev. → Št. prezgodnjih smrti:

SVET **3,5> M**

EVROPA **240.000**

SLOVENIJA **1.300** → **13-krat > letno št. smrti v prometu**

Viri: EEA, 2021; WHO, 2020.

Official Journal
of the European Union

EN
L series

2024/2881

20.11.2024

DIRECTIVE (EU) 2024/2881 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 23 October 2024

on ambient air quality and cleaner air for Europe

(14) It is important that pollutants of emerging concern, such as ultrafine particles, black carbon and elemental carbon, as well as ammonia and the oxidative potential of particulate matter, be measured at monitoring supersites at both rural background locations and urban background locations in order to support scientific understanding of their effects on human health and the environment, as recommended by the WHO. For Member States whose territory is less than 10 000 km^2 measuring at monitoring supersites at urban background locations would be sufficient.

Measuring aerosol absorption for source apportionment and climate change

Griša Močnik, U. Jagodič, L. Pirker, M. Škarabot, M. Kurtjak, K. Vidović, L. Ferrero, B. Visser, J. Röhrbein, E. Weingartner, D.M. Kalbermatter, K. Vasilatou, T. Bühlmann, C. Pascale, T. Müller, A. Wiedensohler, D. Bell, R. Modini, M. Gysel Beer, A. Prevot, L. Drinovec

grisa.mocnik@ung.si

Črni ogljik– absorpcija in segrevanje atmosfere

1 gram = 10 črnih dežnikov

Bond, 2012

1 črn dežnik/ 1 km

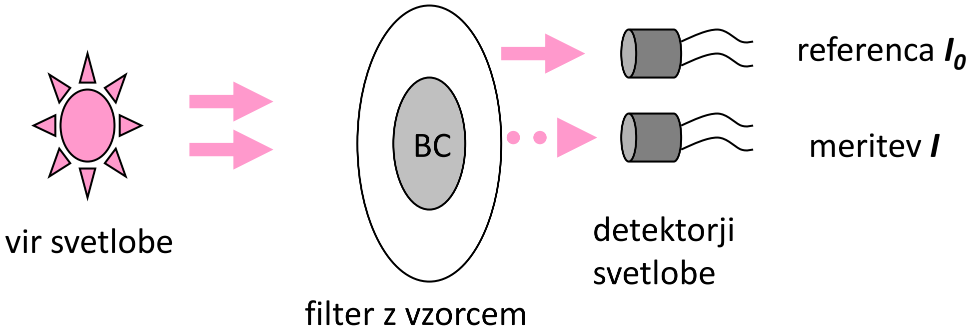
Nekaj **terminologije**

- **Črni ogljik - Black Carbon: masna** koncentracija BC **µgm^{-3}**
  - optična meritev **ekvivalentna** masi **eBC** (filtrski fotometri)

- **absorpcijski koeficient aerosolov** b_{abs} **Mm^{-1}**
  - optična meritev, in-situ, direktna, sledljivo kalibrirana

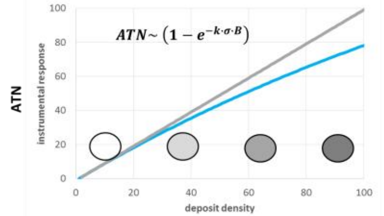
$$\boldsymbol{b_{abs} = BC \cdot MAC}$$

Optična meritev BC: filtrski fotometri



$$ATN = \ln \frac{I_0}{I}$$

$$\boldsymbol{b_{ATN}} \sim \frac{\Delta ATN}{\Delta t} + m_s\, \boldsymbol{b_{sca}}$$

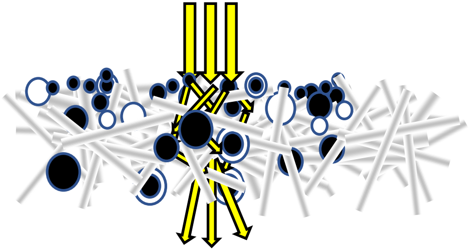


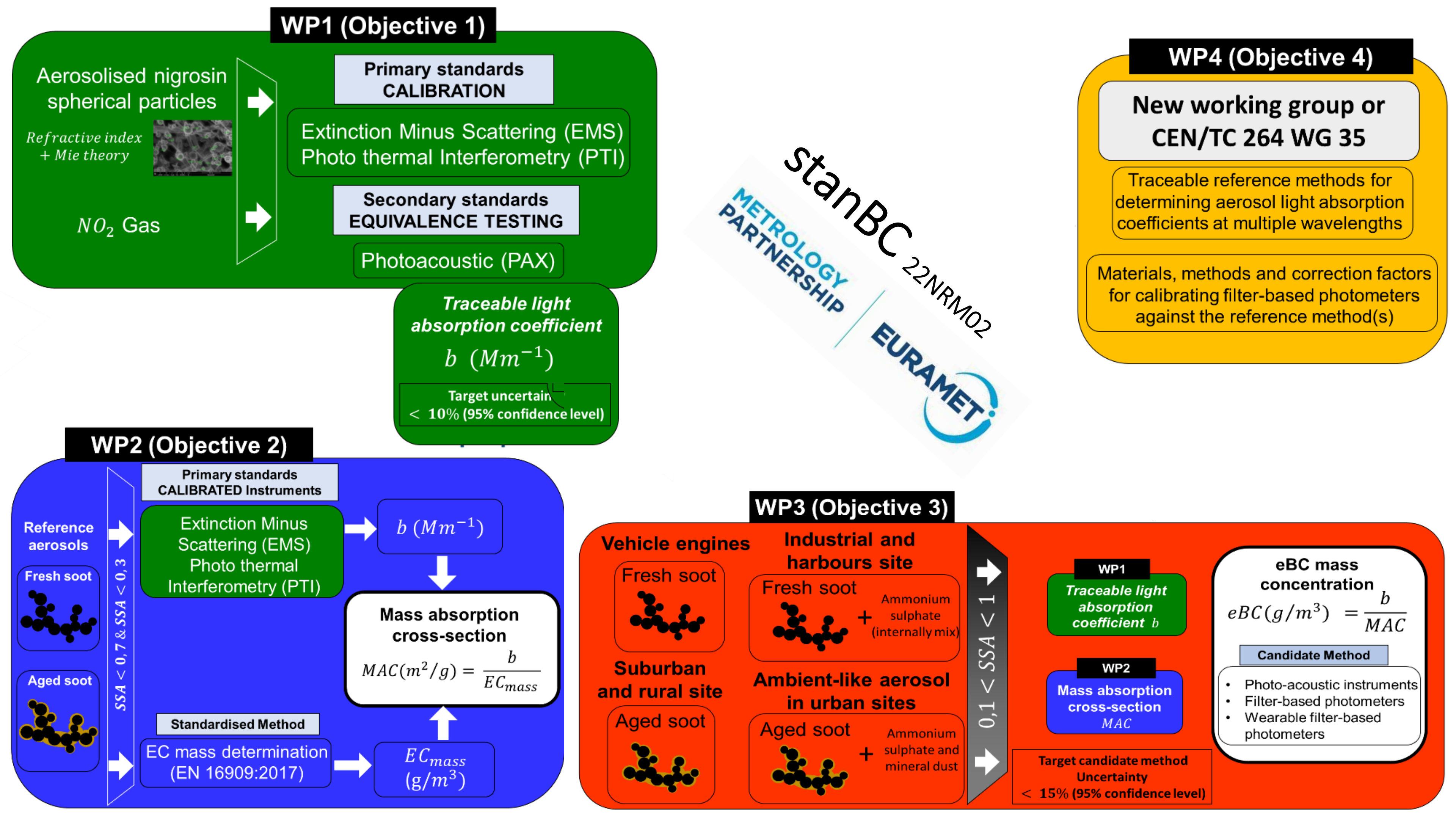
Non-linear response of the detection - saturation

- Vzorčimo **kontinuirno**.
- ***Optična atenuacija*** ~ sprememba ATN.
- Konverzija ***atenuacije*** v ***absorpcijo:***

$$b_{abs} = \frac{b_{ATN}}{C}$$

- Sproti: **minute**

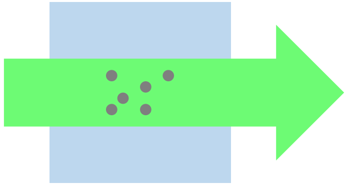




WP1 (Objective 1)
Aerosolised nigrosin spherical particles
Refractive index + Mie theory
NO_2 Gas
Primary standards CALIBRATION
Extinction Minus Scattering (EMS)
Photo thermal Interferometry (PTI)
Secondary standards EQUIVALENCE TESTING
Photoacoustic (PAX)
Traceable light absorption coefficient
$b\ (Mm^{-1})$
Target uncertainty
$<$ 10% (95% confidence level)
stanBC 22NRM02
METROLOGY PARTNERSHIP
EURAMET
WP4 (Objective 4)
New working group or CEN/TC 264 WG 35
Traceable reference methods for determining aerosol light absorption coefficients at multiple wavelengths
Materials, methods and correction factors for calibrating filter-based photometers against the reference method(s)
WP2 (Objective 2)
Reference aerosols
Fresh soot
Aged soot
$SSA < 0,7$ & $SSA < 0,3$
Primary standards CALIBRATED Instruments
Extinction Minus Scattering (EMS)
Photo thermal Interferometry (PTI)
$b\ (Mm^{-1})$
Mass absorption cross-section
$MAC(m^2/g) = \frac{b}{EC_{mass}}$
Standardised Method
EC mass determination (EN 16909:2017)
EC_{mass} (g/m^3)
WP3 (Objective 3)
Vehicle engines
Fresh soot
Industrial and harbours site
Fresh soot
Ammonium sulphate (internally mix)
Suburban and rural site
Aged soot
Ambient-like aerosol in urban sites
Aged soot
Ammonium sulphate and mineral dust
$0,1 < SSA < 1$
WP1
Traceable light absorption coefficient b
WP2
Mass absorption cross-section MAC
Target candidate method Uncertainty
$<$ 15% (95% confidence level)
eBC mass concentration
$eBC(g/m^3) = \frac{b}{MAC}$
Candidate Method
Photo-acoustic instruments
Filter-based photometers
Wearable filter-based photometers

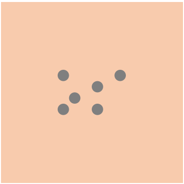
Foto-termična interferometrija

Particle absorb light



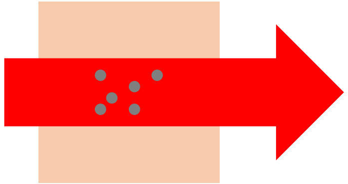
Pump beam intensity: $I=1\ W/mm^2$
Particle temperature: $\Delta T=0.6$ K

Heat transfered to gas



Particle number: $2500\ cm^{-3}$
Air temperature: $\Delta T=8\ \mu K$
Refractive index: $\Delta n=10*10^{-12}$

Measurement of interferometer phase change

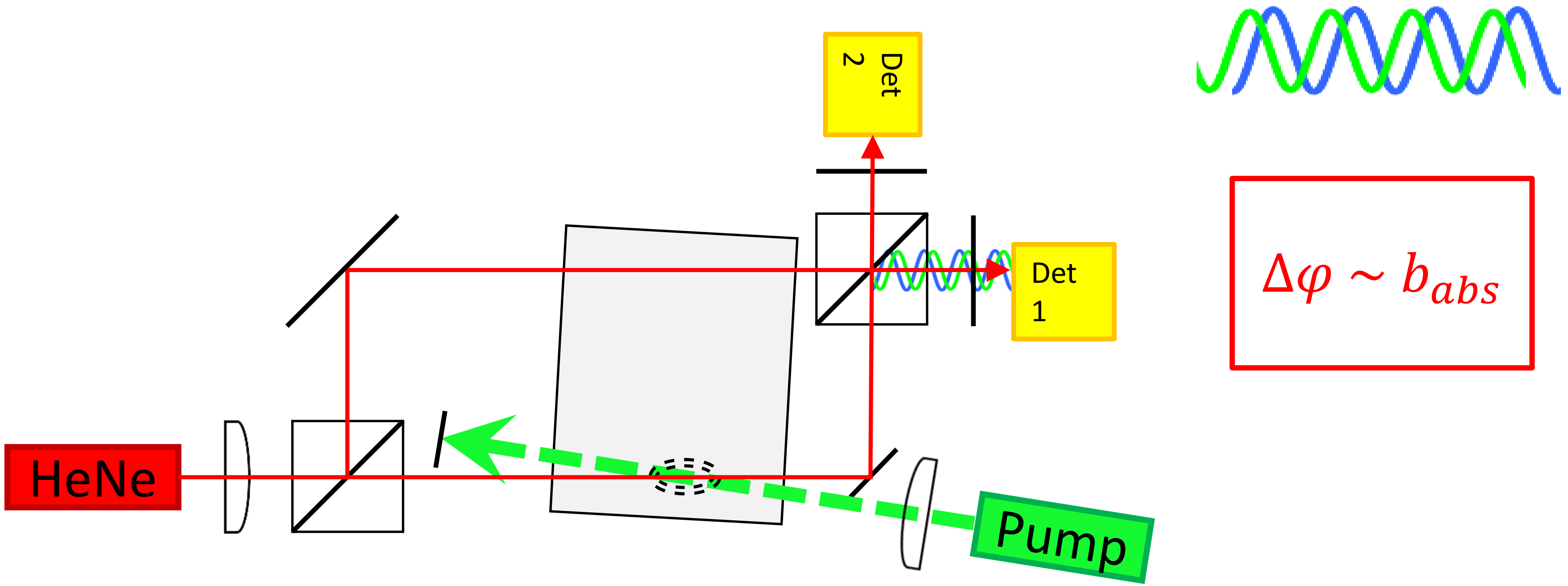


Light path length: $\Delta s=10*10^{-15}$ m
Interferometer phase: $\Delta\phi=0.03\ \mu Rad$

Sprememba faze je proporcionalna absorpcijskemu koeficientu!!

Moosmüller and Arnott, 1996; Sedlacek, 2006; Sedlacek and Lee, 2007; Lee and Moosmüller, 2020; Visser et al., 2020; Drinovec et al., 2022

Mach-Zehnderjev fototermični interferometer



$$\Delta\varphi \sim b_{abs}$$

Courtesy of: E. Weingartner

Članek

Atmos. Meas. Tech., 15, 3805–3825, 2022
https://doi.org/10.5194/amt-15-3805-2022

Atmospheric Measurement Techniques
Open Access
EGU

A dual-wavelength photothermal aerosol absorption monitor: design, calibration and performance

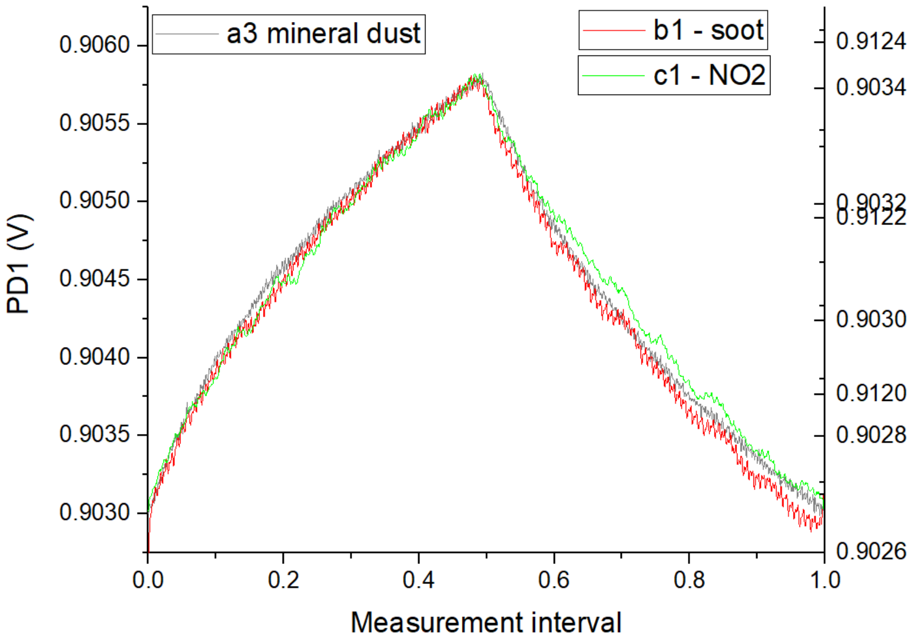
Luka Drinovec[1,2,3], Uroš Jagodič[1,2], Luka Pirker[2,4], Miha Škarabot[2], Mario Kurtjak[5], Kristijan Vidović[6], Luca Ferrero[7], Bradley Visser[8], Jannis Röhrbein[8], Ernest Weingartner[8], Daniel M. Kalbermatter[9], Konstantina Vasilatou[9], Tobias Bühlmann[9], Celine Pascale[9], Thomas Müller[10], Alfred Wiedensohler[10], and Griša Močnik[1,2,3]

https://doi.org/10.5194/amt-15-3805-2022

Photo-Thermal Aerosol Absorption Monitor
PTAAM

532 nm & **1064 nm**
450 nm & **808 nm**
450, 520, 785 nm

Foto-termični signal – ni vpliva velikosti aerosolov



Volume mode diameter

- saje: 250 nm
- puščavski prah: 5 µm

- **Meritev ni odvisna od velikosti delcev!**
- Kalibracija s plini.
- Merimo lahko delce od saj do puščavskega prahu.

Kalibraija: 450 and 532 nm – sledljiva do primarnih standardov

Instrument response denpends on:

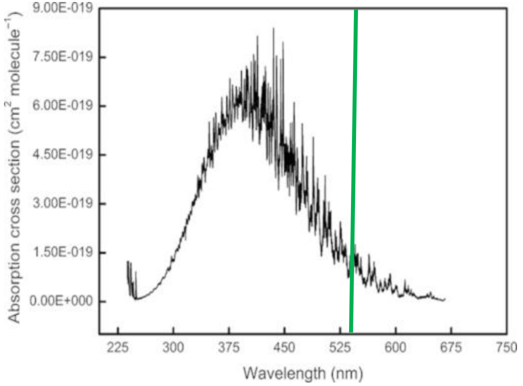
- Pump beam intensity
- Overlap between pump and probe beams

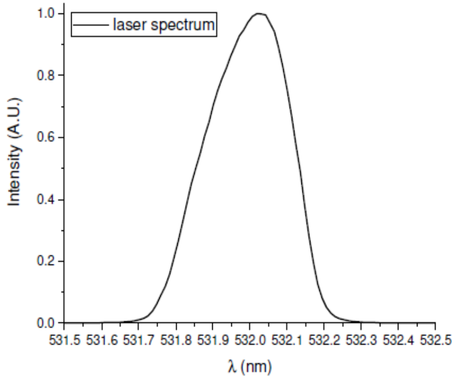
-> instrument must be **calibrated**.

traceably calibrated
METAS permeation NO_2 generator
(Haerri et al. 2017)

450 and 532 nm channel calibration:

- Using absorbing gas: $\mathbf{NO_2}$
- Absorption cross-section = $1.47*10^{-19}$ cm^2 @ 532 nm

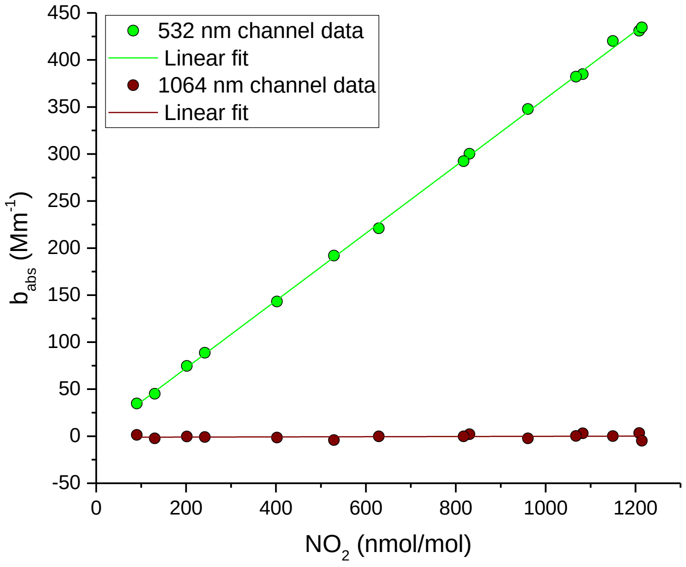




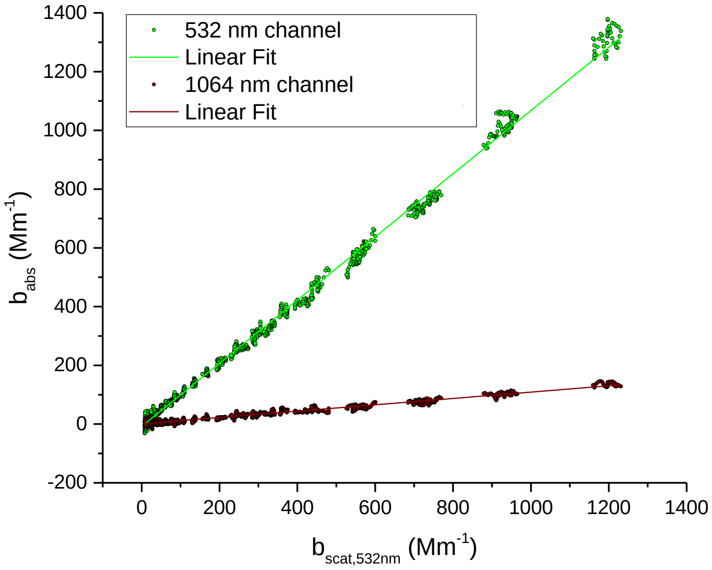
Drinovec et al., 2022

Linearni odziv

NO_2



Nigrosin



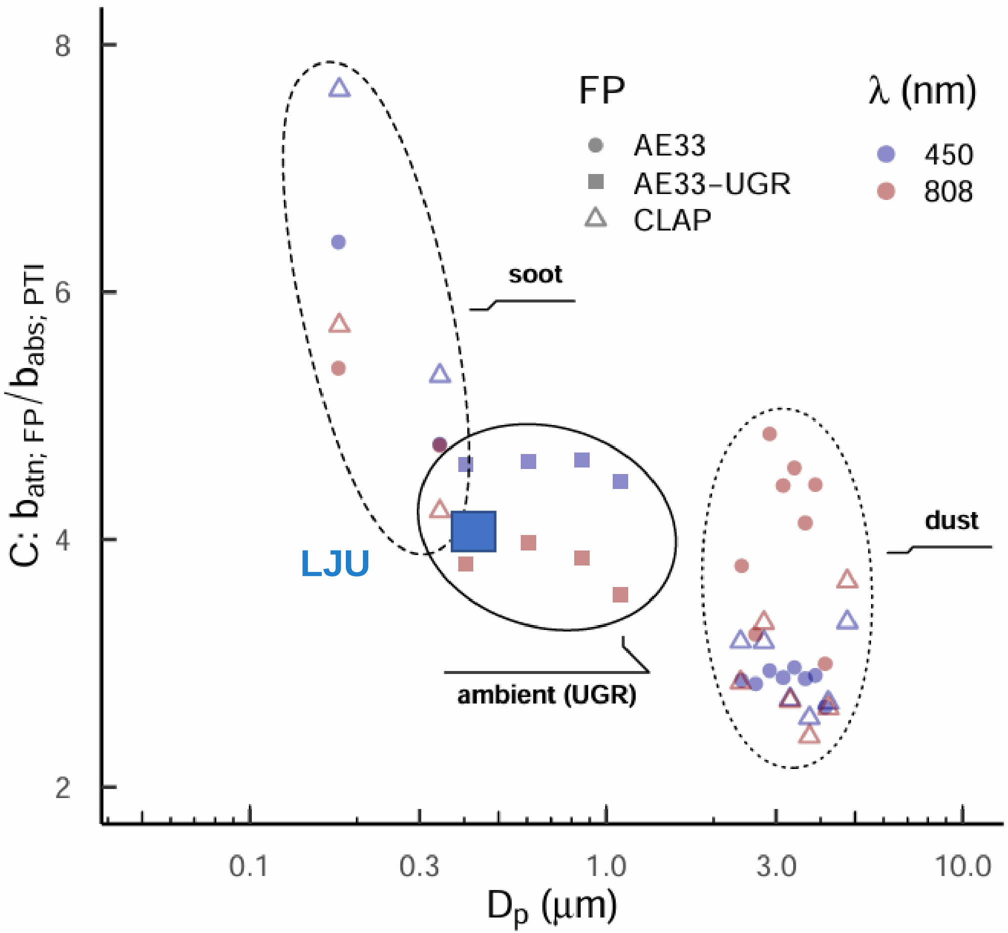
Drinovec et al., 2022

Negotovost meritve

	sources of uncertainty	uncertainty	
A	NO_2 amount fraction	2.0%	Haerri, 2017
B	NO_2 absorption cross-section	2.0%	Vandaele, 2002; Orphal, 2003
C	Mie calc. & nigrosin refractive index	2.0%	Drinovec, 2022
D	Mie calc. & particle size distribution	4.0%	Drinovec, 2022
E	scattering & absorbing gases	1.0%	Drinovec, 2022
F	stability of instrument response	3.0%	Drinovec, 2022
	combined uncertanties		
	b_{abs} @ 450 nm	4.2%	A, B, E, F
	b_{abs} @ 808 nm	6.2%	A, B, C, D, E, F
	AAE	10.4%	C, D, E, F

Yus Diez et al., 2025

Kalibracija

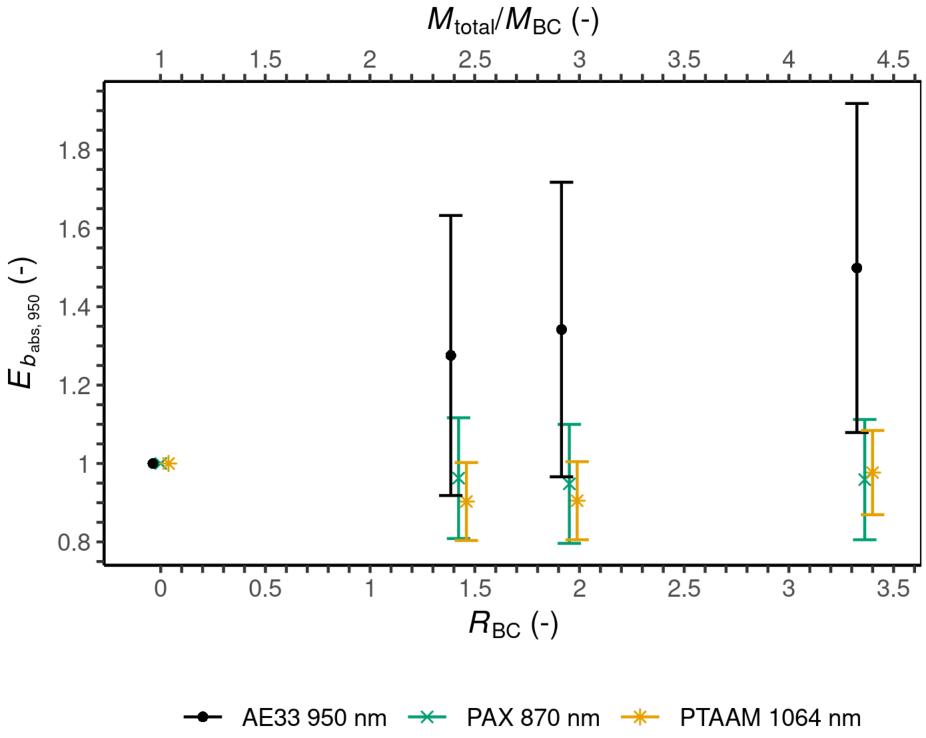


Yus Diez et al., 2025

Primerjava

- **PTAAM** is the **only** traceable instrument
- **no artefacts**, independent of SSA
- commercially available

- possibility of further intercomparisons
- stanBC:
  - METAS **NO2 permeator**
  - \+ **PTAAM** or transfer standard PAX



Kalbermatter et al., 2022

Sklepi

- absorpcija aerosolov
- **sledljiva kalibracija**
- **linearni** odziv & **ni artefaktov**
- **zelo nizka negotovost** meritve -> **referenčni** inštrument za absorpcijo
- **LOD** @ 450 nm, **0.15 Mm^{-1}** @ 100 s avg

Vpliv prometa, kurjenja lesa in industrije na sestavo in toksičnost delcev PM

K. Glojek[1,6], V. Dinh Ngoc Thuy[2], S. Weber[2], G. Uzu[2], M. Manousakas[3,4], R. Elazzouzi[2], K. Džepina[1], S. Darfeuil[2], P. Ginot[2], J.–L. Jaffrezo[2], R. Žabkar[5], J. Turšič[5], A. Podkoritnik[1] and **G. Močnik**[1]

1 Univerza v Novi Gorici, Center za raziskave atmosfere(CRA), Ajdovščina, 5270, Slovenia

2 University of Grenoble Alpes, CNRS, INRAE, IRD, Grenoble INP, IGE, Grenoble 38000, France

3 Paul Scherrer Institute (PSI), Laboratory of Atmospheric Chemistry, Villigen 5232, Switzerland

4 NCSR DEMOKRITOS Institute of Nuclear and Particle Physics, Agia Paraskevi, 15341, Greece

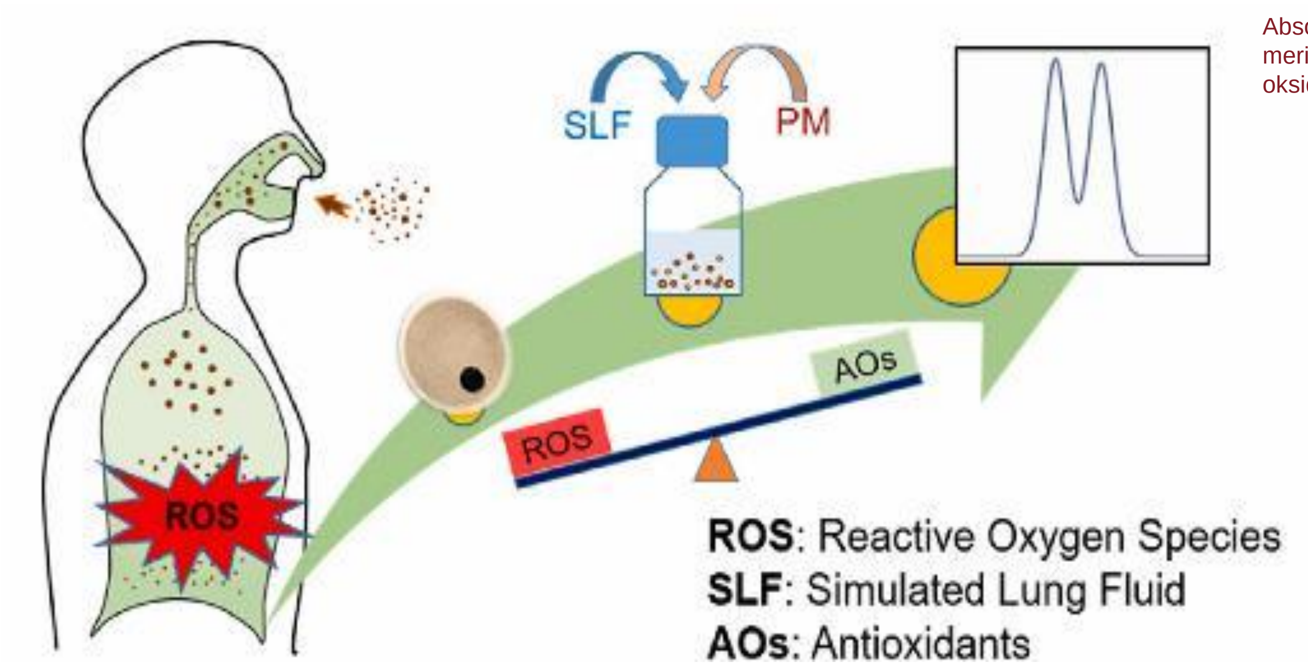
5 Slovenian Environment Agency, Ljubljana 1000, Slovenia

6 Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, 08034, Spain

Foto: Občina Kanal ob Soči

Merilo vpliva na zdravje: Oksidativni Potencial (OP)

PM delci kot povzročitelji oksidativnega stresa (Weber et al, 2021).



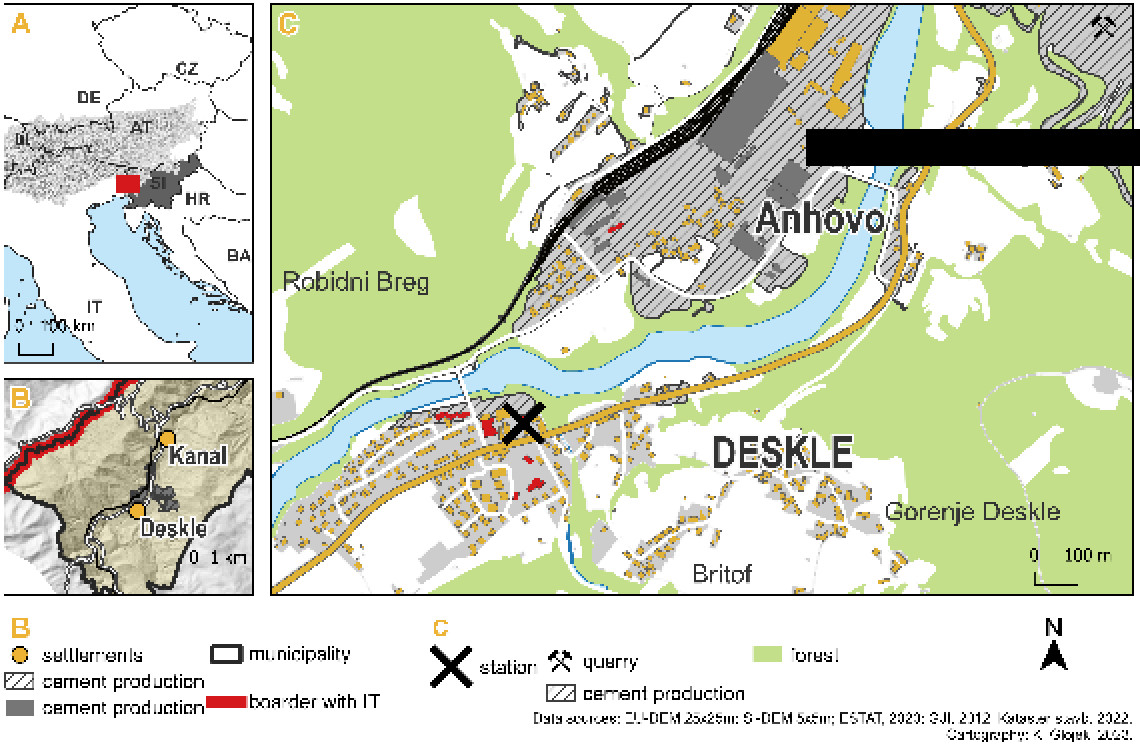
Absorbcijske meritve porabe oksidantov

Različna občutljivost na kemijske spojine in velikost PM.

- Dithiothreitol (**DDT**)
- Askorbinska kislina (**AA**)

Vir: Shahpoury et al., 2022.

Območje proučevanja: Kanal ob Soči



Glojek et al., 2024

Meritve na strehi OŠ Deskle

zima 2020/21 **pomlad 2021** **poletje 2021** **jesen 2021**

PM_{10} & črni ogljik

PM_{10}

Digitel DHA-80

24-urni filtri

Črni ogljik

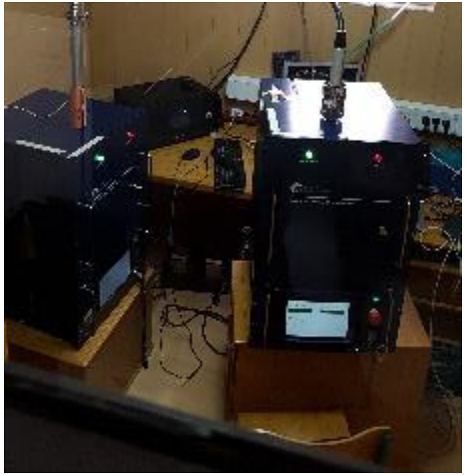
Aethalometer AE33:

1-min meritve

Določanje virov

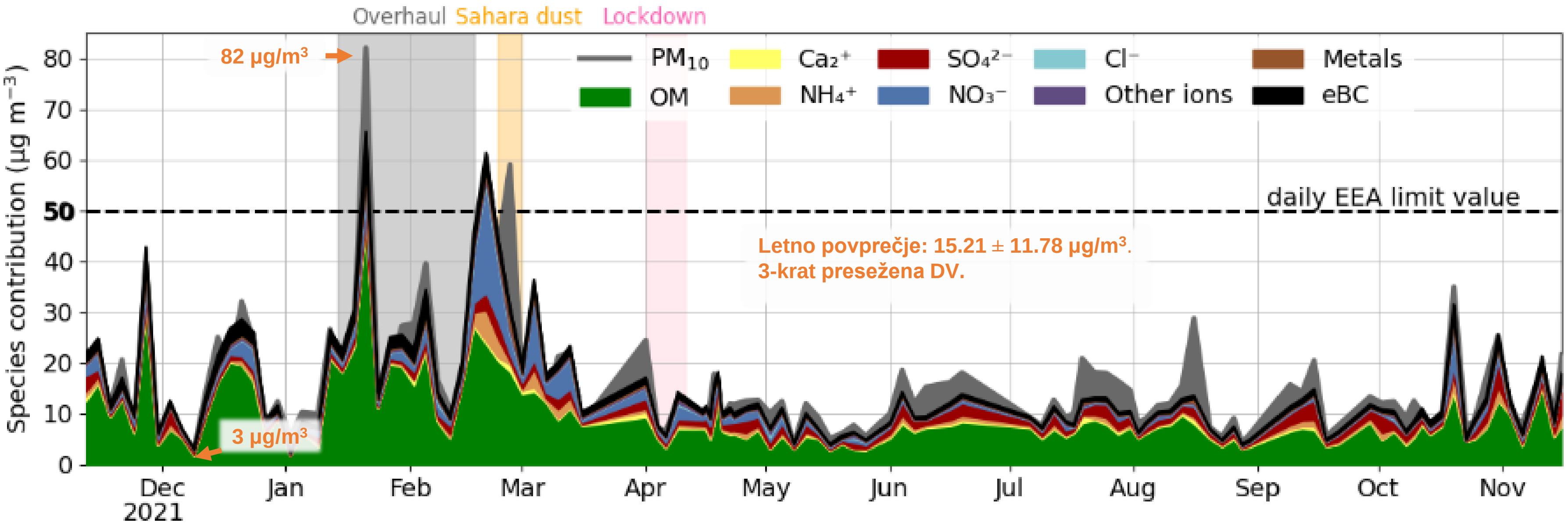
Kemijska sestava filtrov PM_{10}

Črni ogljik



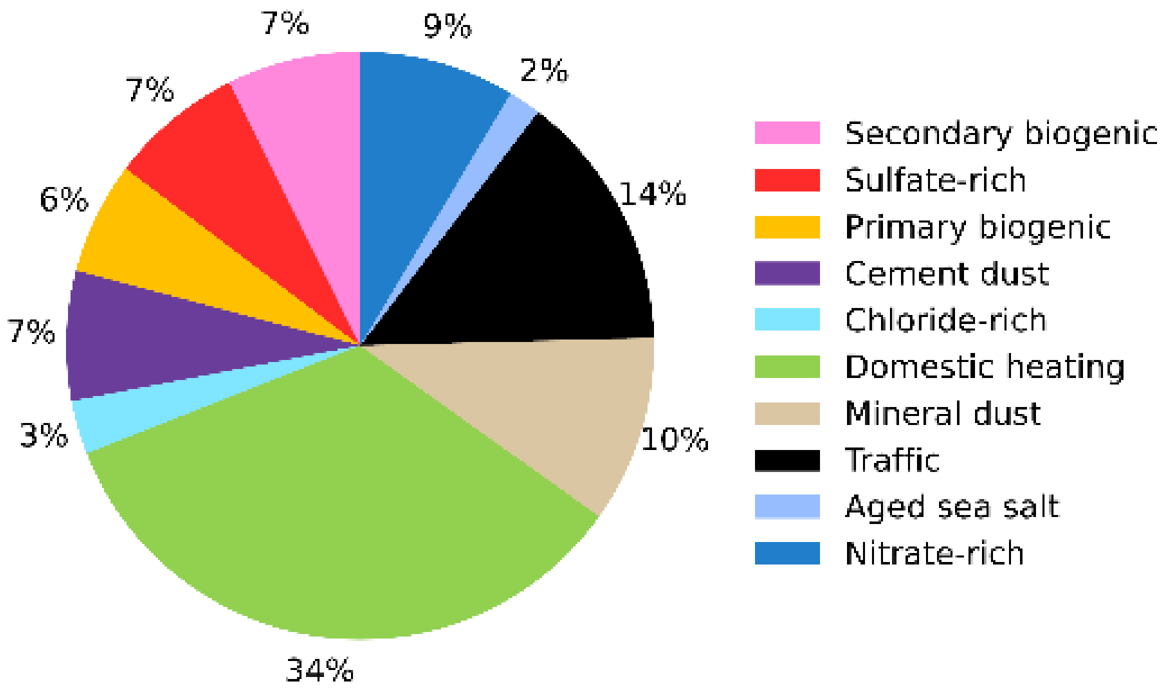
Pozitivna Matrična Faktorizacija (PMF)

PM_{10} in kemijska sestava



Glojek et al., 2024

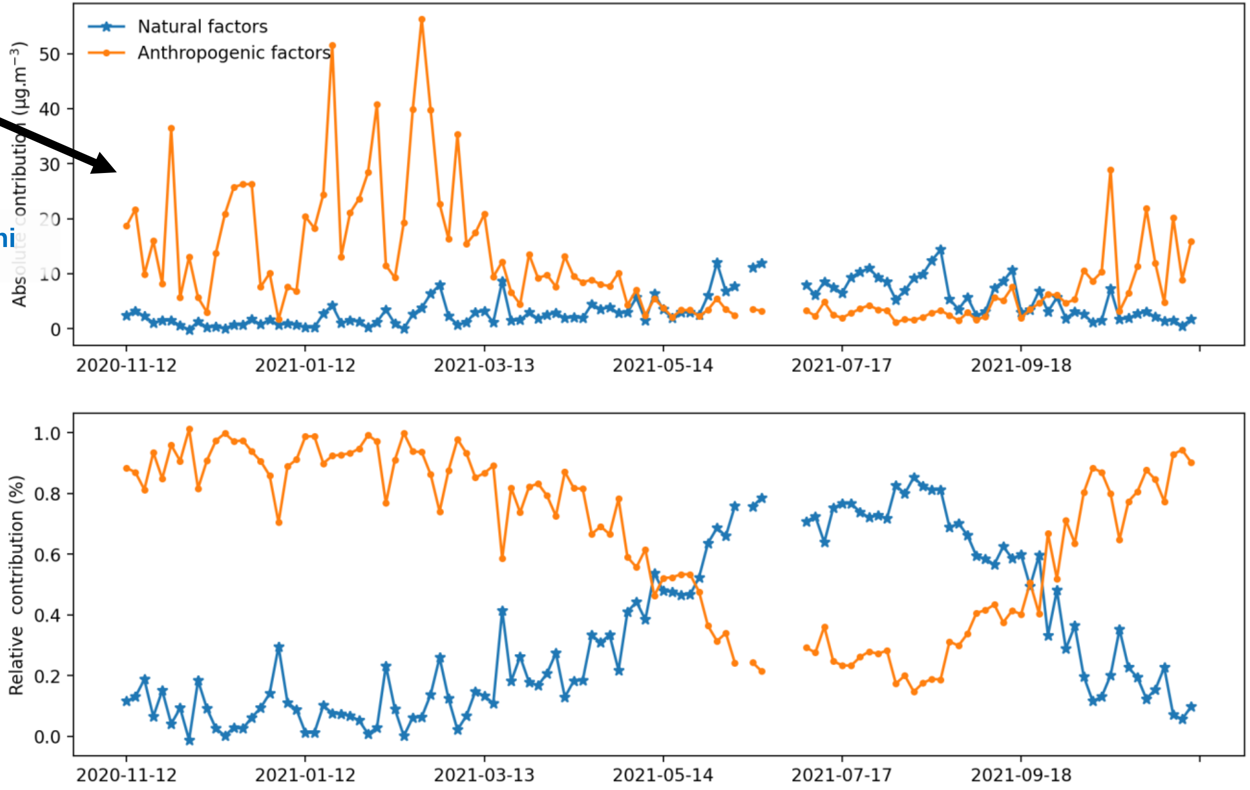
PMF: viri PM_{10}



Glojek et al., 2024

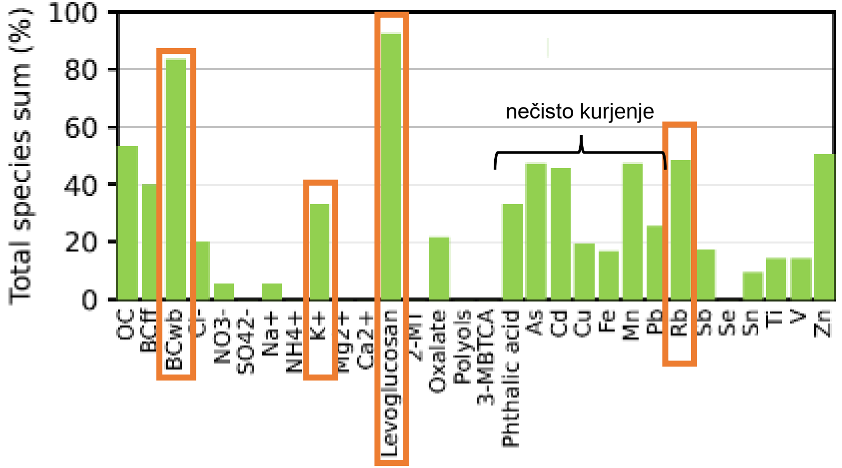
Naravni proti antropogeni viri

Antropogeni > > naravni



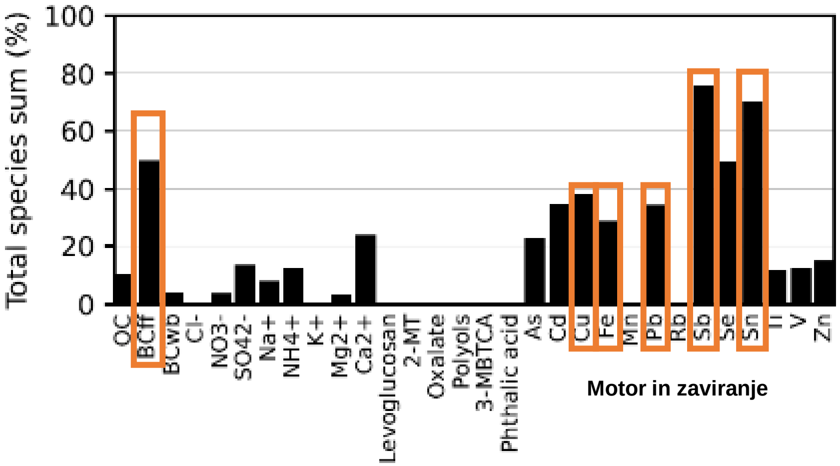
Glojek et al., 2024

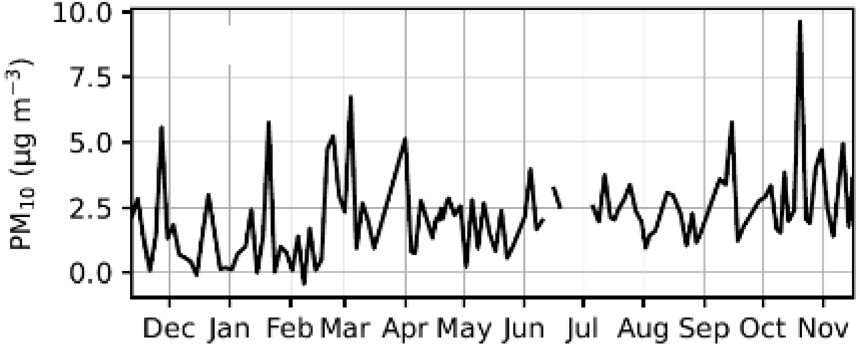
Zgorevanje biomase

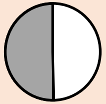


Glojek et al., 2024

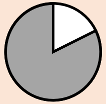
Promet





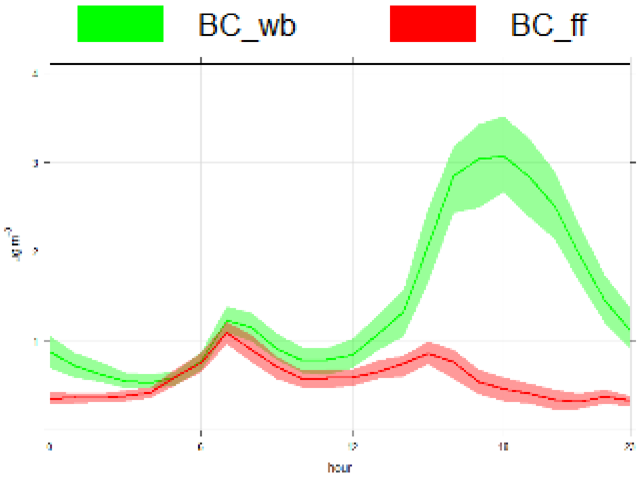


v industrijsko cono Anhovo

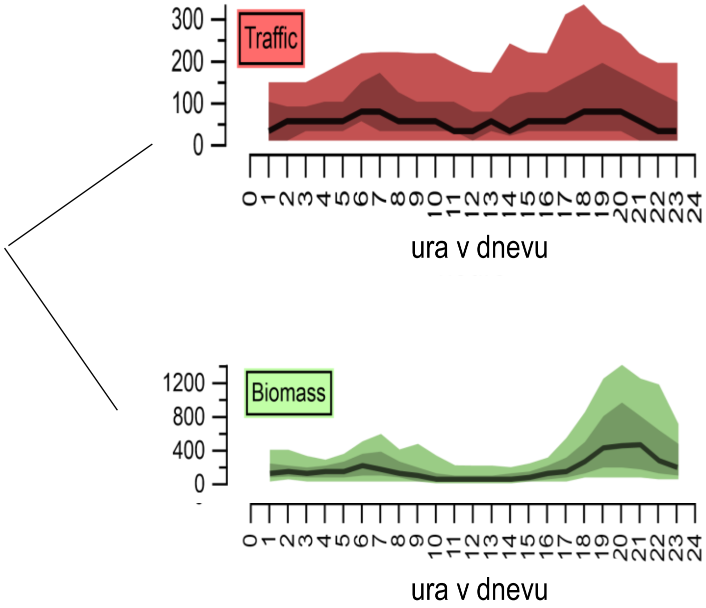


Glojek et al., 2024

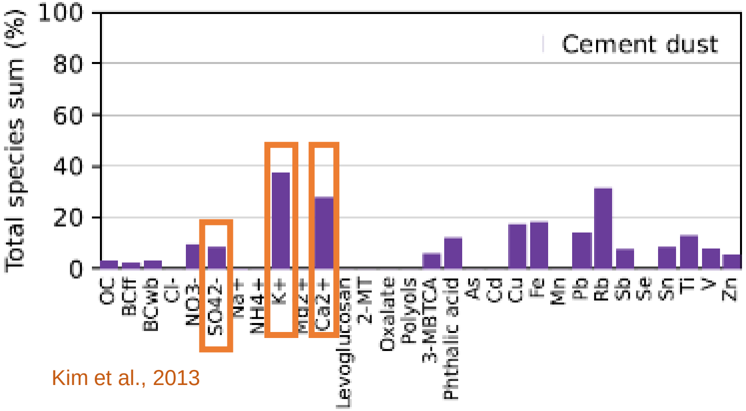
Zgorevanje biomase & Promet



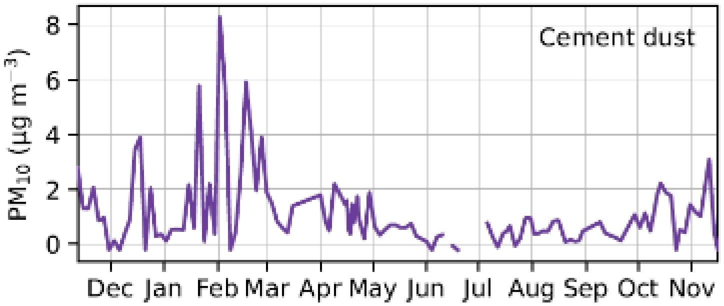
Kovine v sledovih



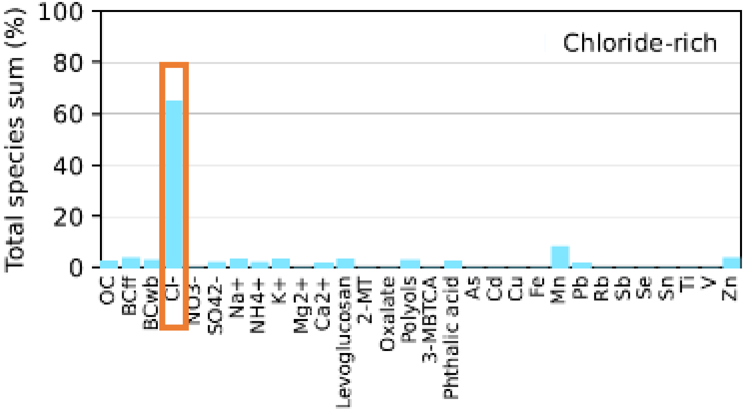
Industrijska vira

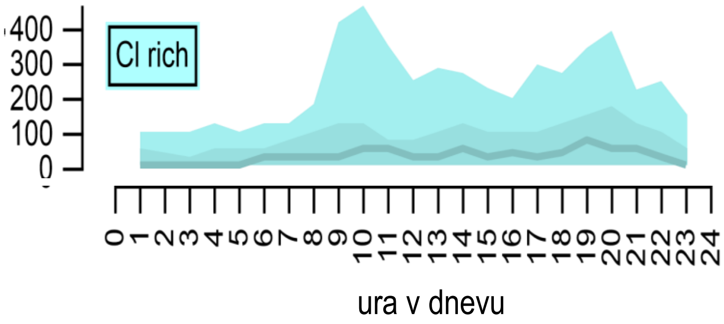


Kim et al., 2013



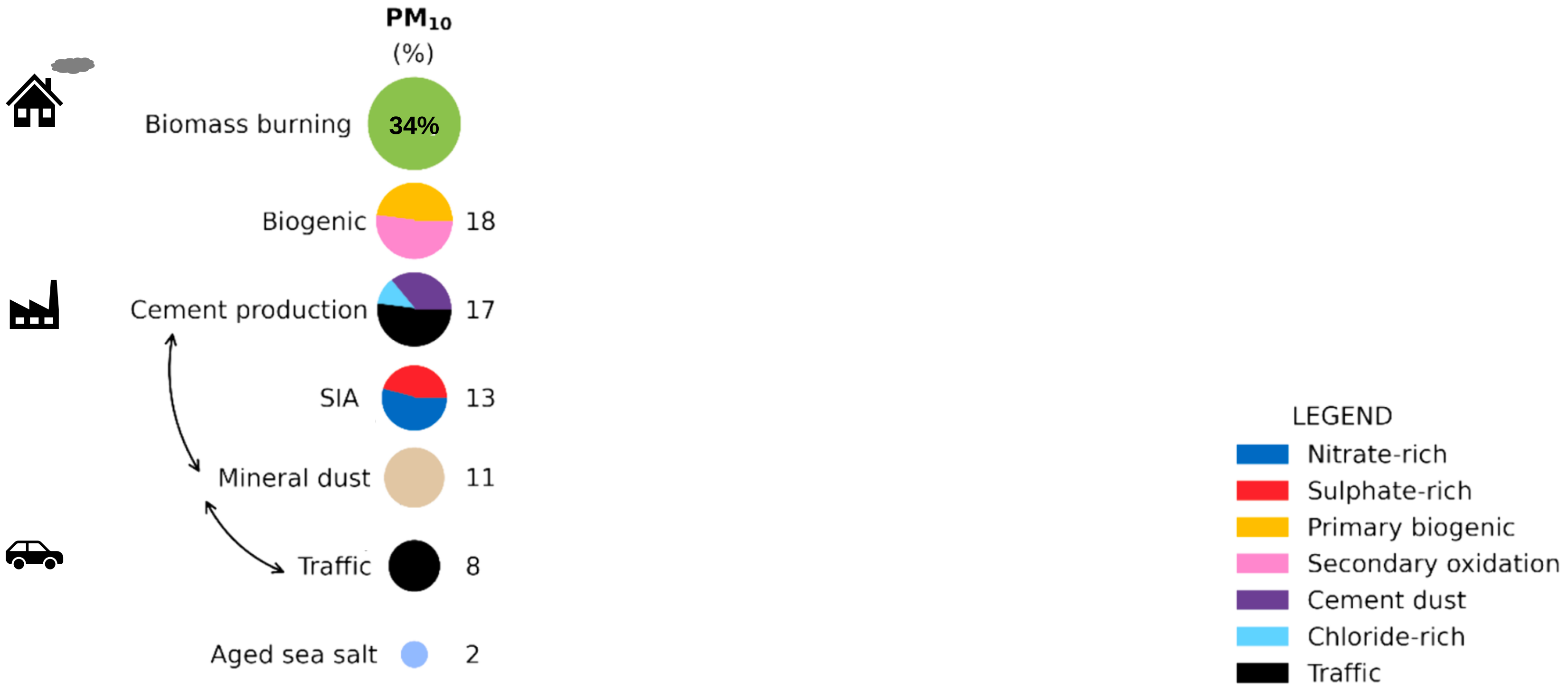
Kim et al., 2013





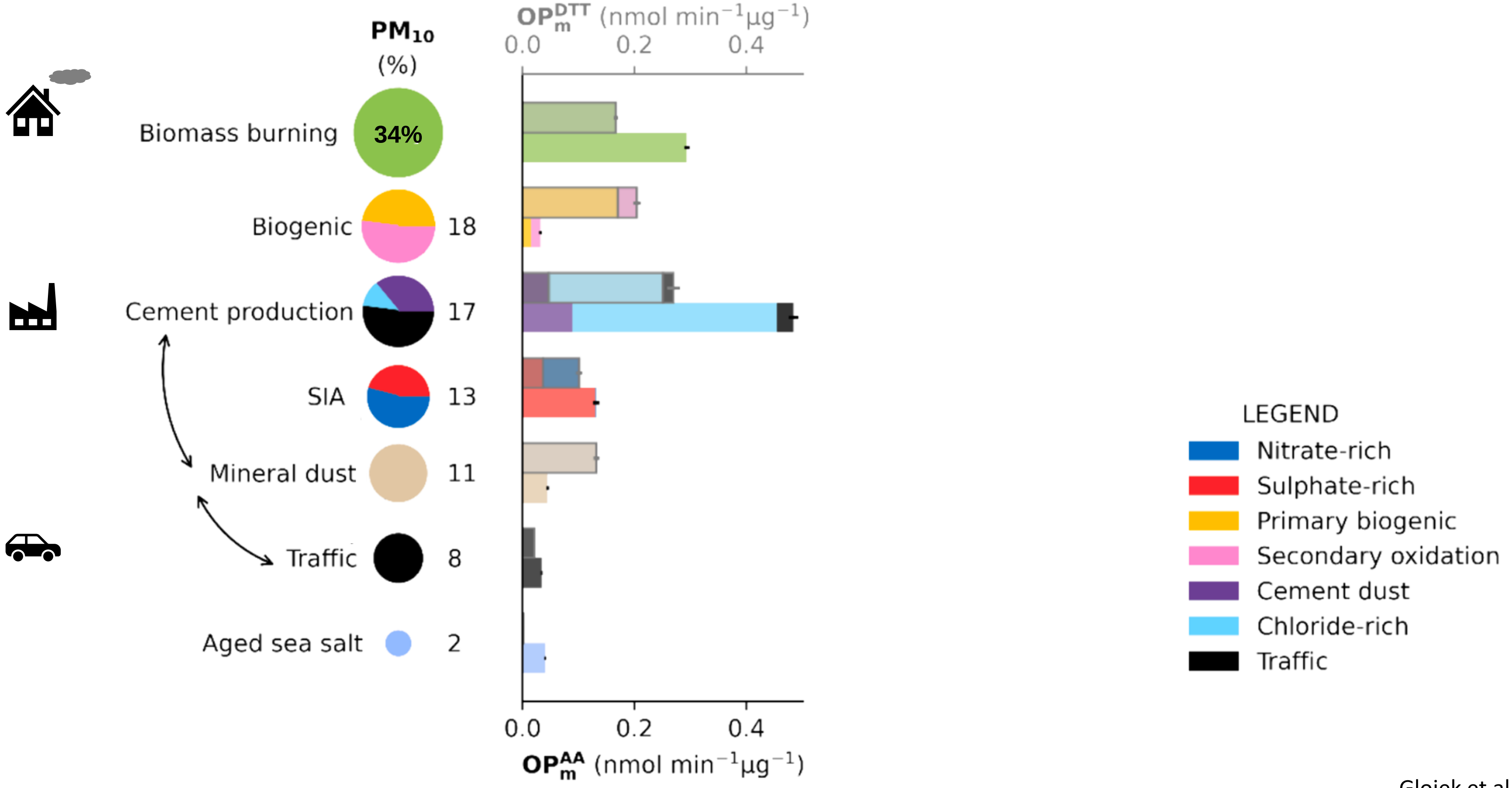
Glojek et al., 2024

Skupni prispevek virov k PM_{10}



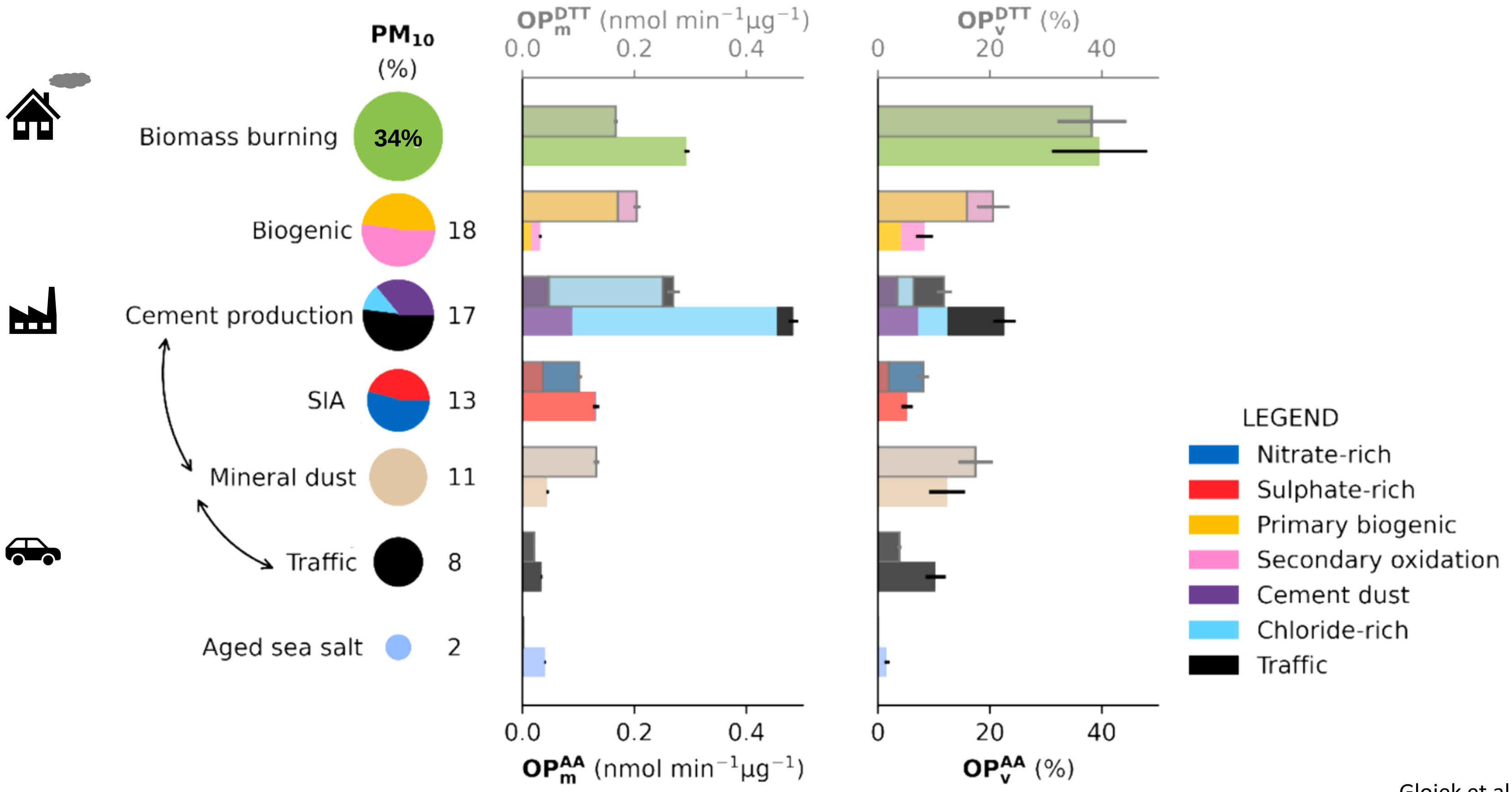
Glojek et al., 2024

Skupni prispevek virov k OP_m



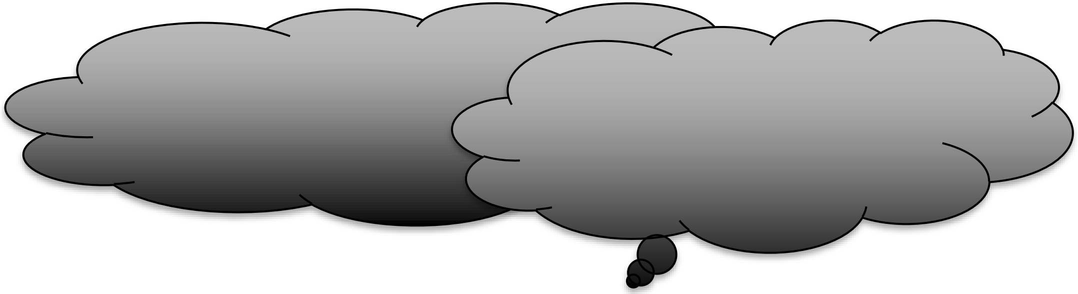
Glojek et al., 2024

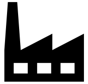
Skupni prispevek virov k OP_V



Glojek et al., 2024

Povzetek



- **PM_{10} ≈ druga alpska območja.** (Herich et al., 2014)
- Najpomembnejši viri: 
- **OP ≈ med najvišjimi v Evropi.** (Daellenbach et al., 2020; Weber et al., 2021; Borlaza et al., 2021b)
- Nenavaden vir bogat **s kloridi,** z **visokim OP_m**. 
- Nadaljne raziskave:
  - primerjava rezultatov z drugimi uporabljenimi metodami;
  - vzorčenje resuspendiranega prahu na različnih lokacijah po dolini.

Hvala!

OBČINA
KANAL OB SOČI

IGE
Institut des Géosciences de l'Environnement

PSI

HAZE
INSTRUMENTS

REPUBLIKA SLOVENIJA
MINISTRSTVO ZA OKOLJE IN PROSTOR
AGENCIJA REPUBLIKE SLOVENIJE ZA OKOLJE

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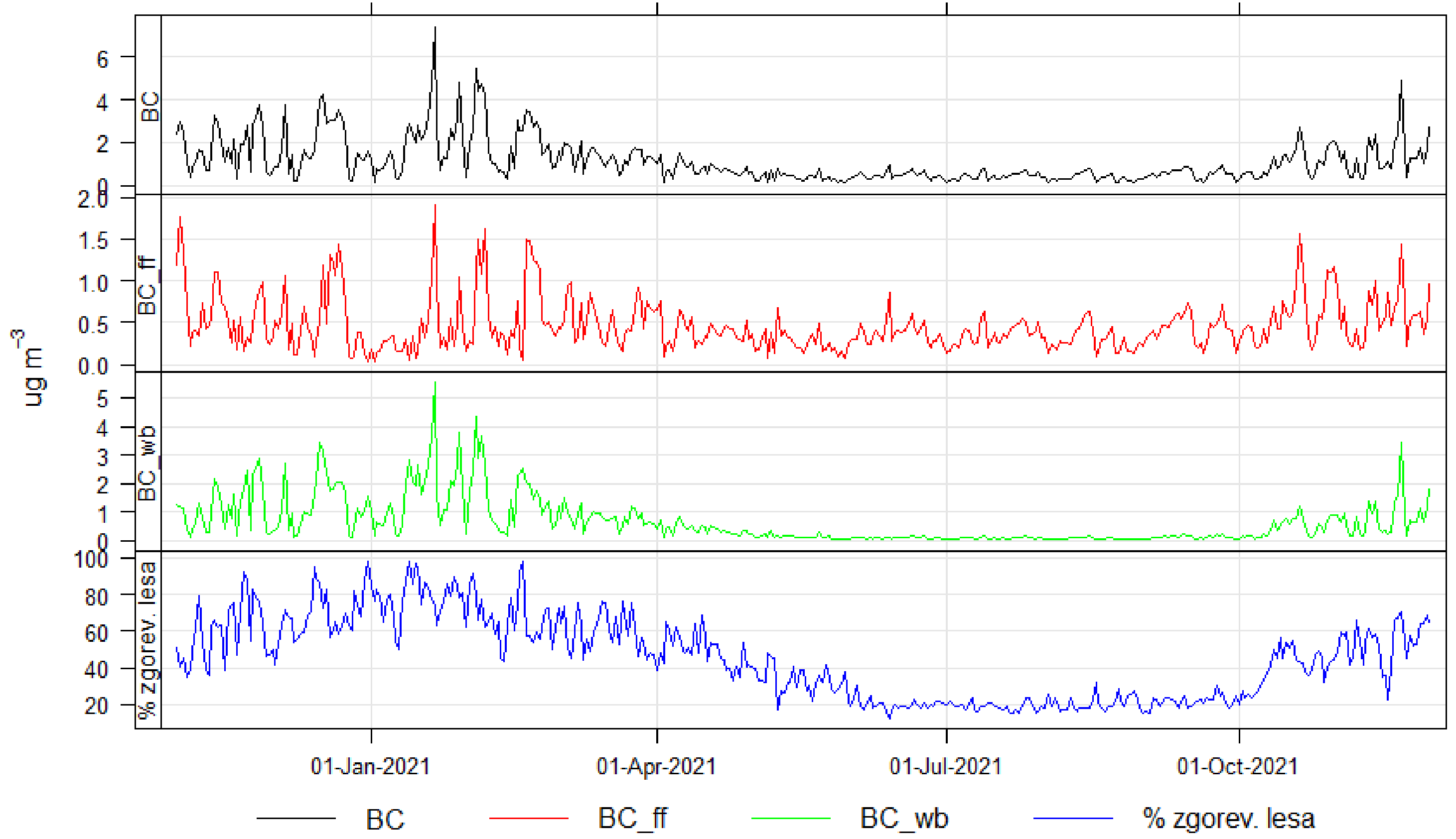
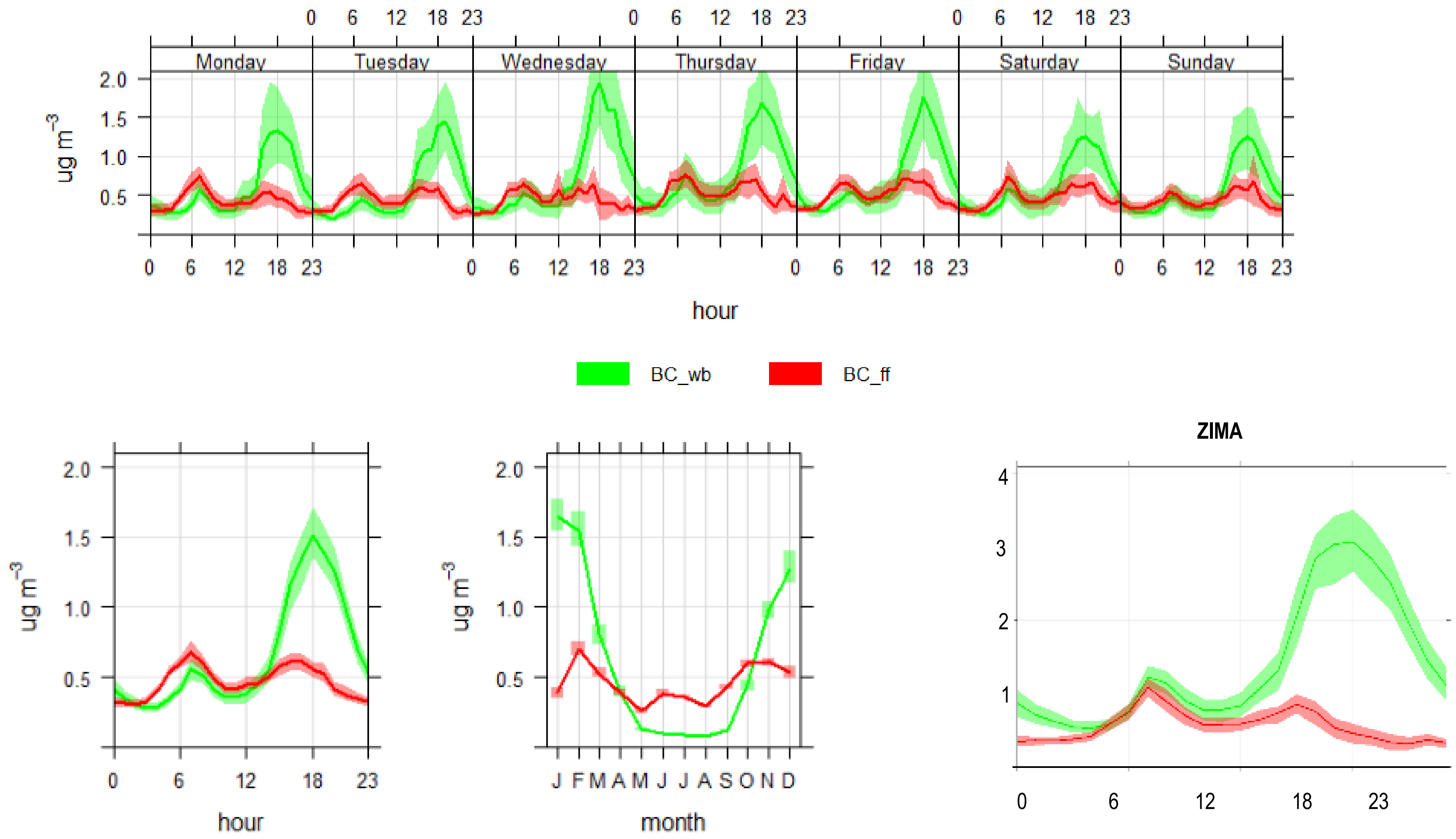
kristina.glojek@ung.si

Merjeni parametri

parameter	metoda
organski ogljik	analiza OC/EC, EN 16909:2017 in Cavalli et al. (2010)
črni ogljik, BC	meritve z Aethalometrom, Drinovec (2015), Sandradewi (2008)
ioni in lahke organske spojine $NO3^-$, NO2-, $SO4^{2-}$, Cl^-, $NH4^+$, Na^+, K^+, Mg^{2+}, Ca^{2+} glukonat, glikolat, propionat, format, MSA, propionat, piruvat, cis-pinonska kislina, 2-ketobutirična kisl., gliksolat, pinska kisl., butirat, 4-oksoheptanojska, glutarična, adipična, sksinična, malična kislina, tartarat, malonična, maleična kislina, oksalat, pinonat, azelaična, ftalična, vanilična kislina, 3-MBTCA, sebakična kisl., citrat	ionska kromatografija IC-MS v PM10, drugače enako kot EN 16913:2017 Chevrier (2016a), Chevrier et al., (2016b)
kovine Ag Al As Bi Cd Cs Cu Fe Mn Mo Ni Pb Rb Sb Sc Se Sn Ti V Zn	masni spektrometer z induktivno sklopljeno plazmo ICP-MS Chevrier (2016a), Chevrier et al., (2016b)
polioli in sladkorji oksalat, eritriol, ksilitol, arabitol, sorbitol, manitol, trealoza, levoglukozan, manozan, galaktozan, glukoza	tekočinska kromatografija visoke ločljivosti s pulzno amperometrično detekcijo HPLC-PAD Chevrier (2016a), Chevrier et al., (2016b)
oksidativni potencial	ditiotreitiol - DTT, askorbinska kislina - AA Weber et al. (2018) in reference tam

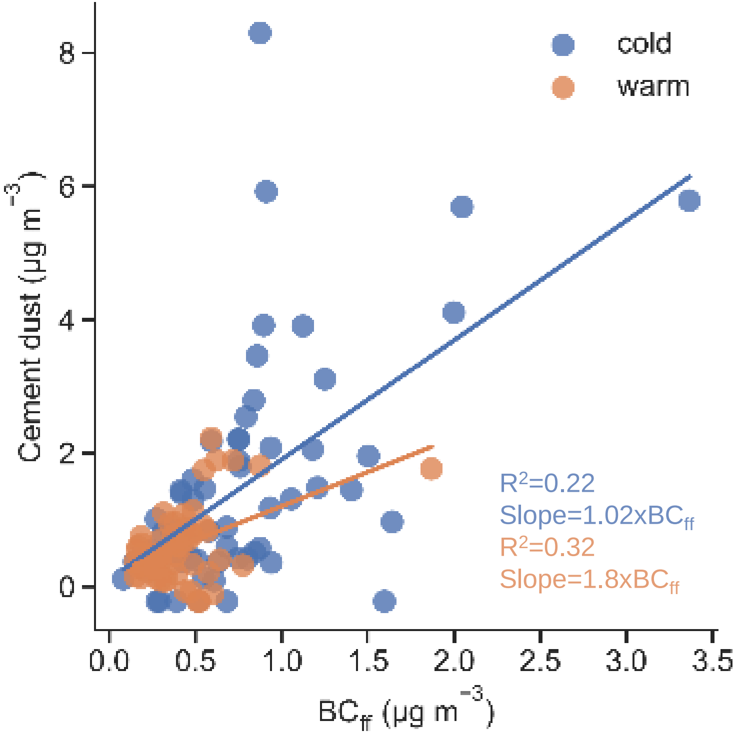
Viri črnega ogljika

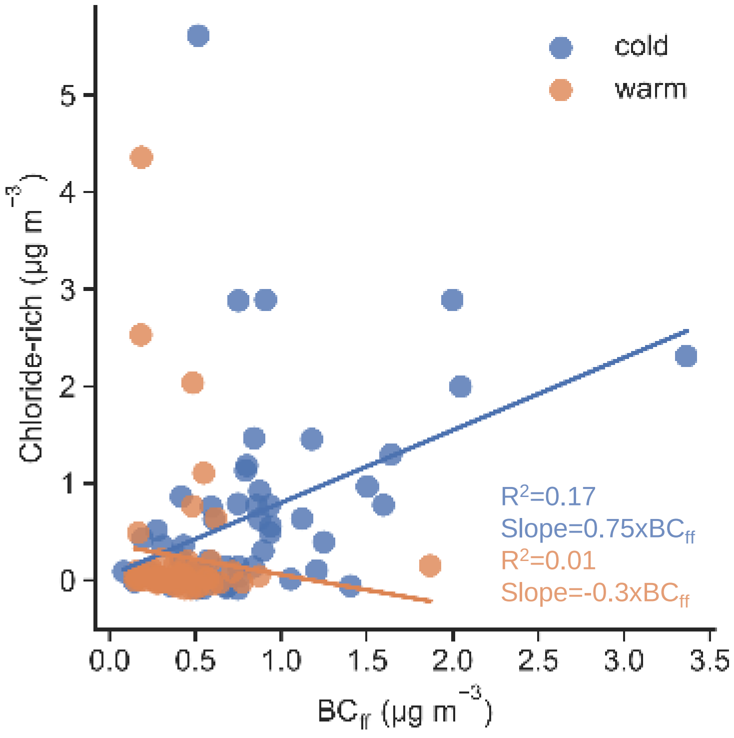



Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
ug m^{-3}
hour
BC_wb
BC_ff
month
ZIMA

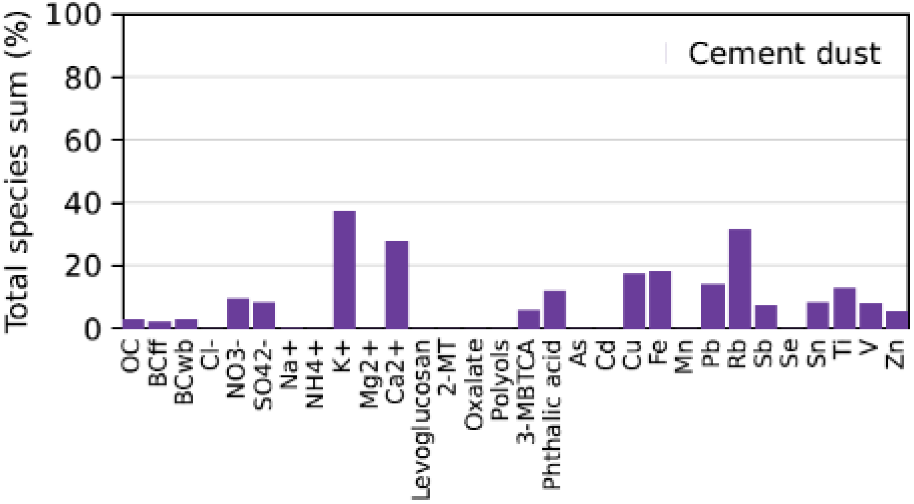
Antropogeni viri

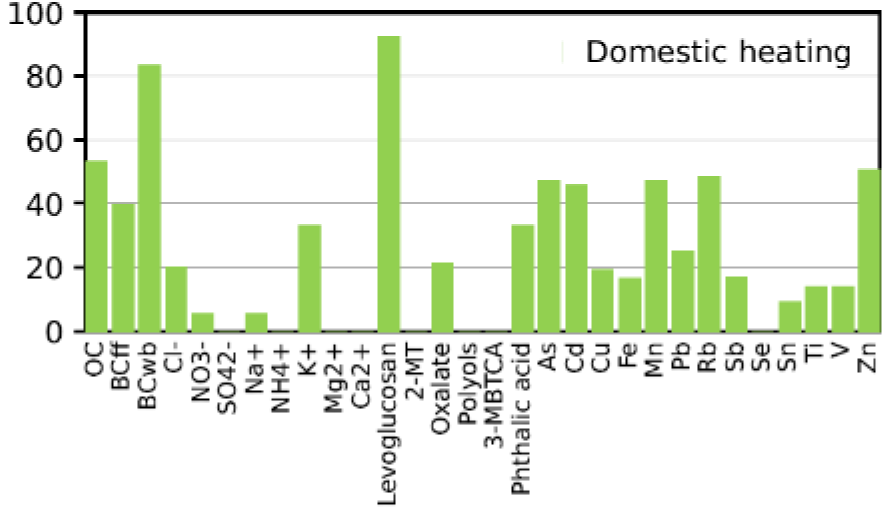
Vir: mehanski procesi

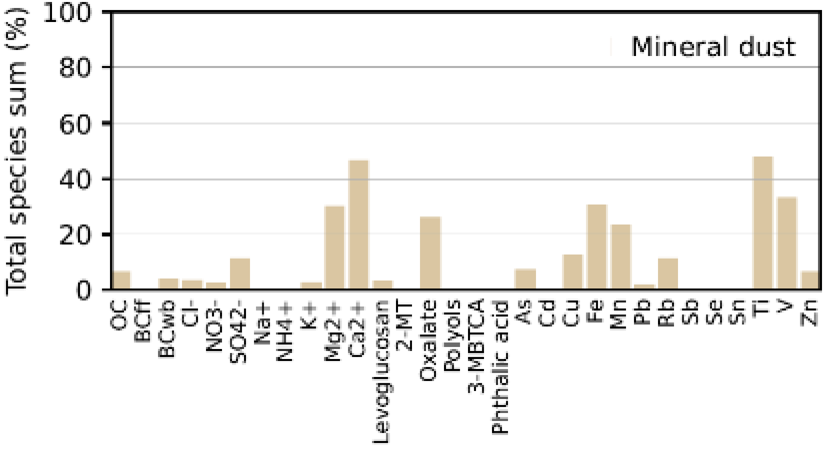


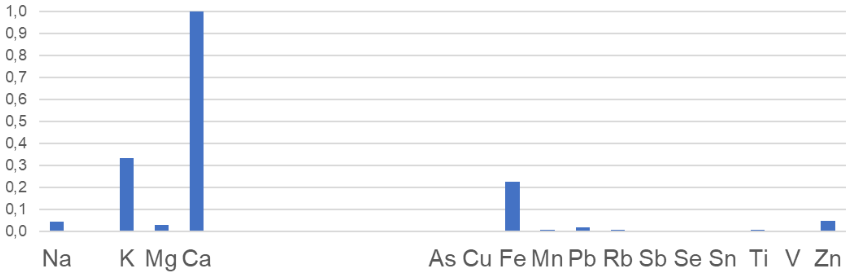



GO ZT-516
GO EB 084

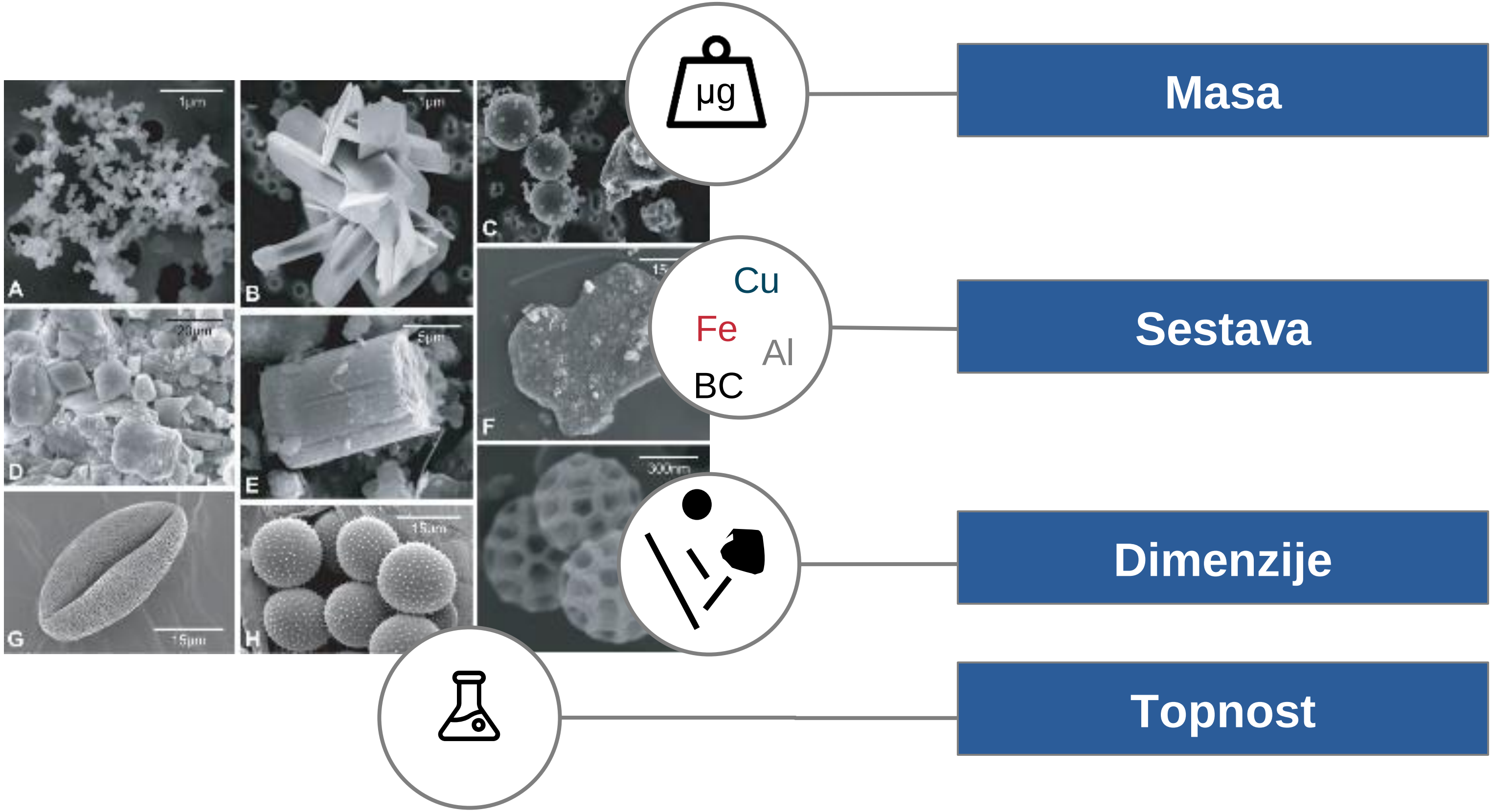

Cement dust
Total species sum (%)
100
80
60
40
20
0
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn


Domestic heating
100
80
60
40
20
0
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn


Mineral dust
Total species sum (%)
100
80
60
40
20
0
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn


1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
Na
K
Mg
Ca
As
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn

Različne lastnosti



Onesnaženje s PM delci

Največja okoljska grožnja zdravju (WHO, 2021).

PM “škodljivost” ↔ Cu Fe BC Al sestava ↔

Alpske doline in problem kakovosti zraka

- Visoki izpusti:

(e. g. Herich et al., 2014; Glojek et. al., 2022)

- Meteorologija.
- Pomanjkanje raziskav specifičnih ind. virov.
- Proizvodnja cementa:

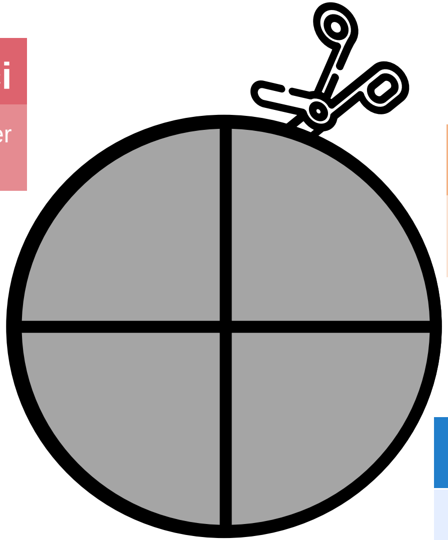
↑ Visoki izpusti in potencialna toksičnost.

(Kim et al., 2003; Rovira et al., 2018; Chen et al., 2022; Ervik et al., 2022).


Foto: Občina Kanal ob Soči

Kemijske analize

Vsak 3. filter, skupaj 120



Ogljični delci

OC/EC, Thermooptical analyzer

Ioni

Ion chromatography (IC).

Organski sledilci

IC and HPLC-PAD.

Kovine

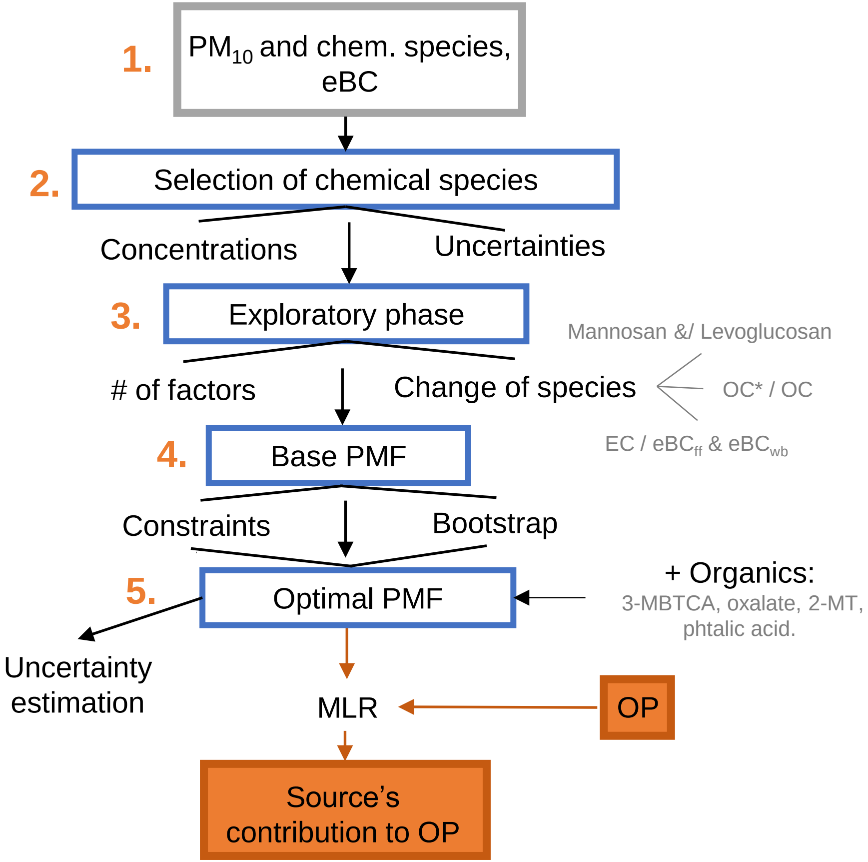
Inductively coupled plasma mass spectroscopy (ICP-MS).

Oksidativni potencial

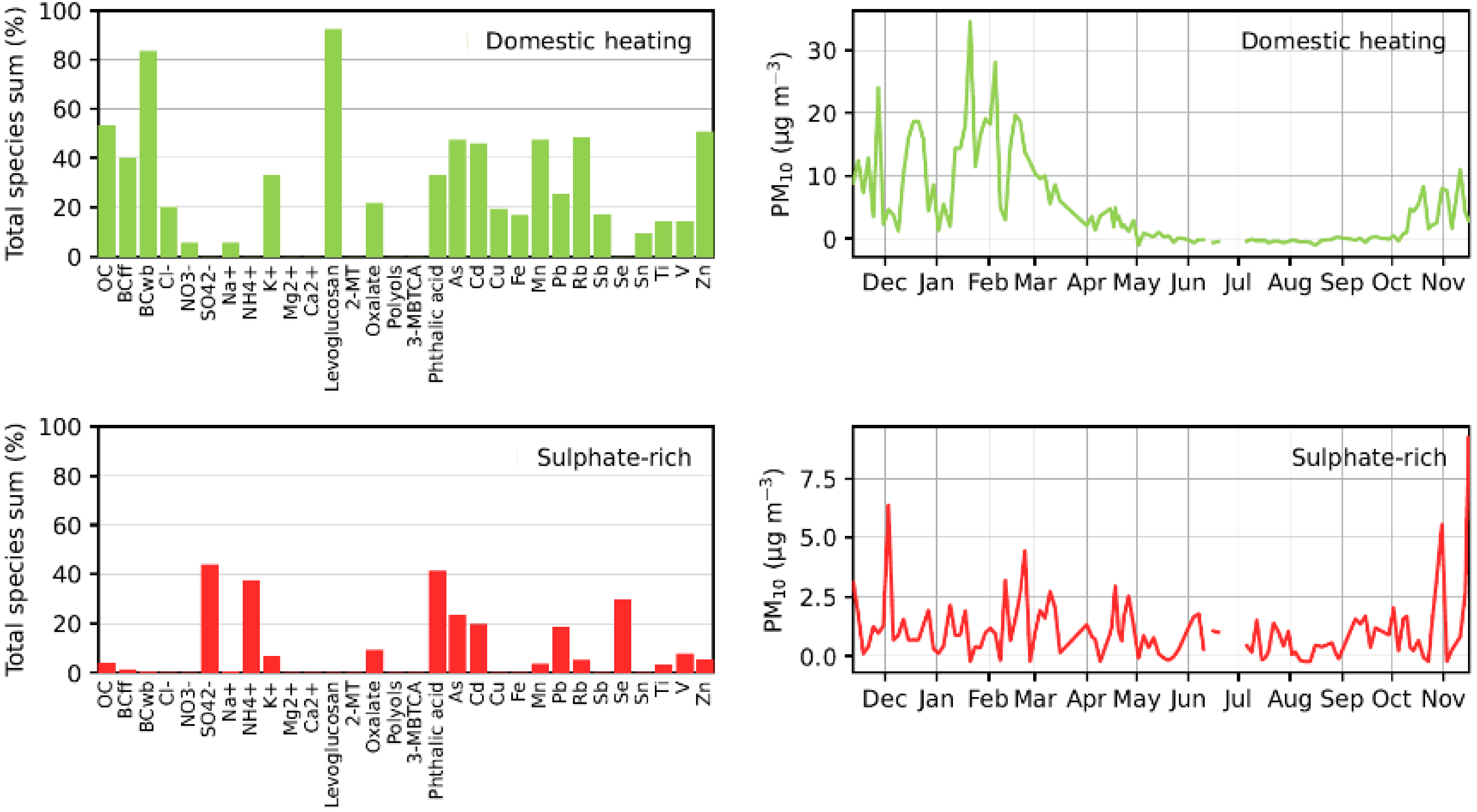
Askorbinska kislina (AA), dithiothreitol (DTT)

Pozitivna Matrična Faktorizacija (PMF): koraki

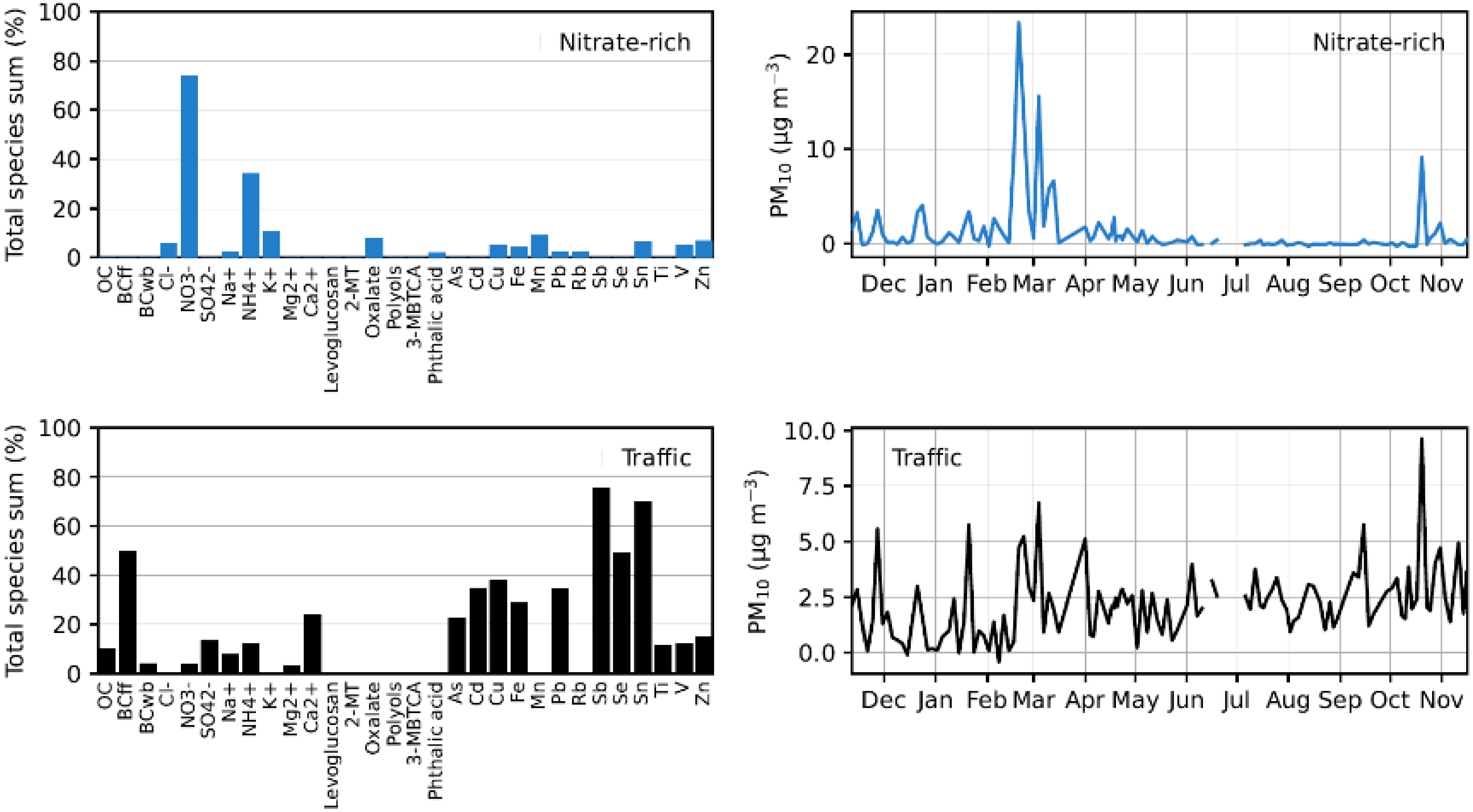
Software: EPA PMF 5.0



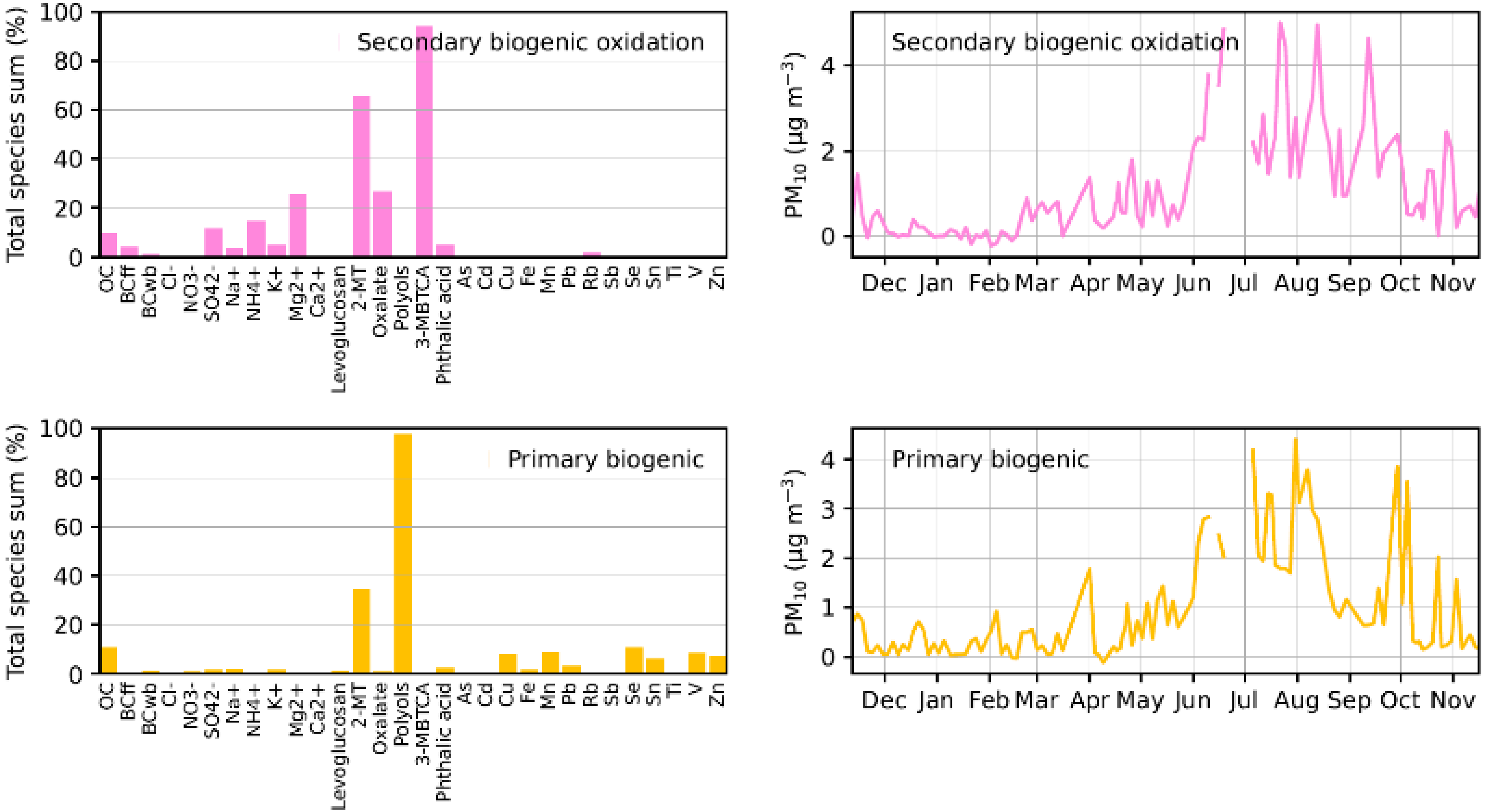
LEGEND:
eBC – equivalent black carbon
OP – oxidative potential
MLR - multiple linear regression



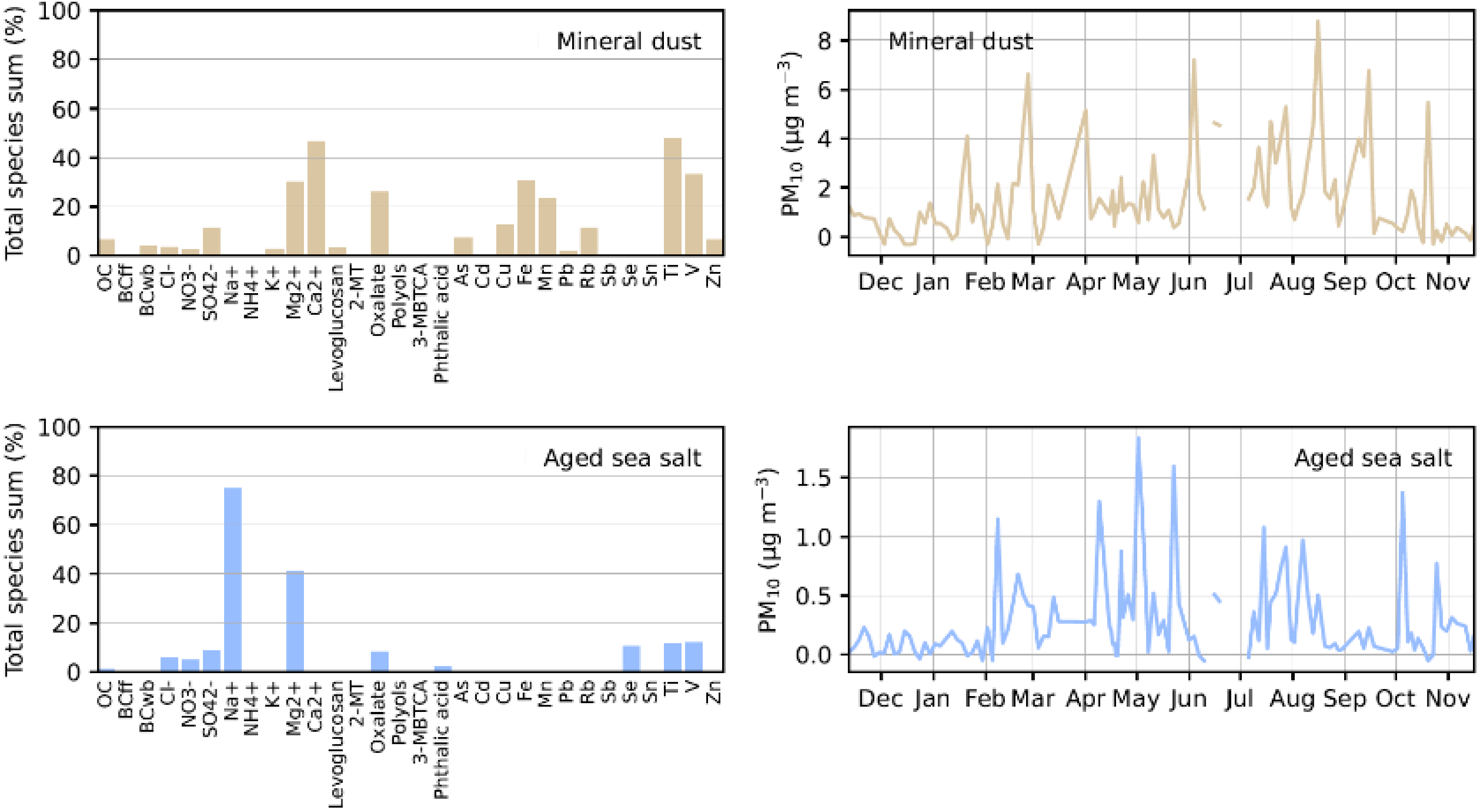
Domestic heating
Total species sum (%)
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn
Domestic heating
PM_{10} (µg m^{-3})
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Sulphate-rich
Total species sum (%)
Sulphate-rich
PM_{10} (µg m^{-3})



Nitrate-rich
Total species sum (%)
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn
PM10 (µg m−3)
Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov
Traffic

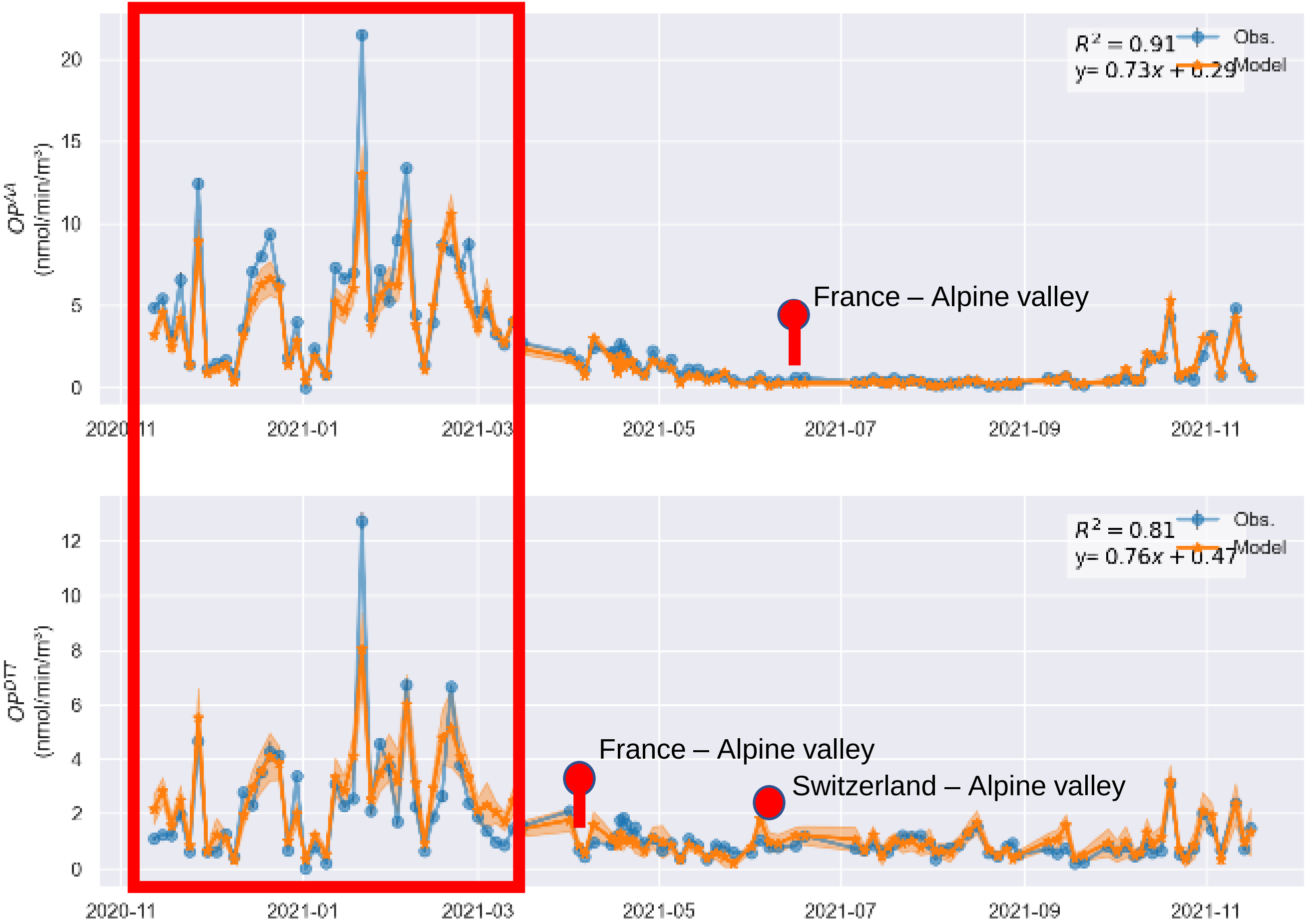


Secondary biogenic oxidation
Total species sum (%)
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn
PM10 (μg m−3)
Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov
Primary biogenic



Mineral dust
Aged sea salt
Total species sum (%)
PM10 (µg m−3)
OC
BCff
BCwb
Cl-
NO3-
SO42-
Na+
NH4+
K+
Mg2+
Ca2+
Levoglucosan
2-MT
Oxalate
Polyols
3-MBTCA
Phthalic acid
As
Cd
Cu
Fe
Mn
Pb
Rb
Sb
Se
Sn
Ti
V
Zn
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov

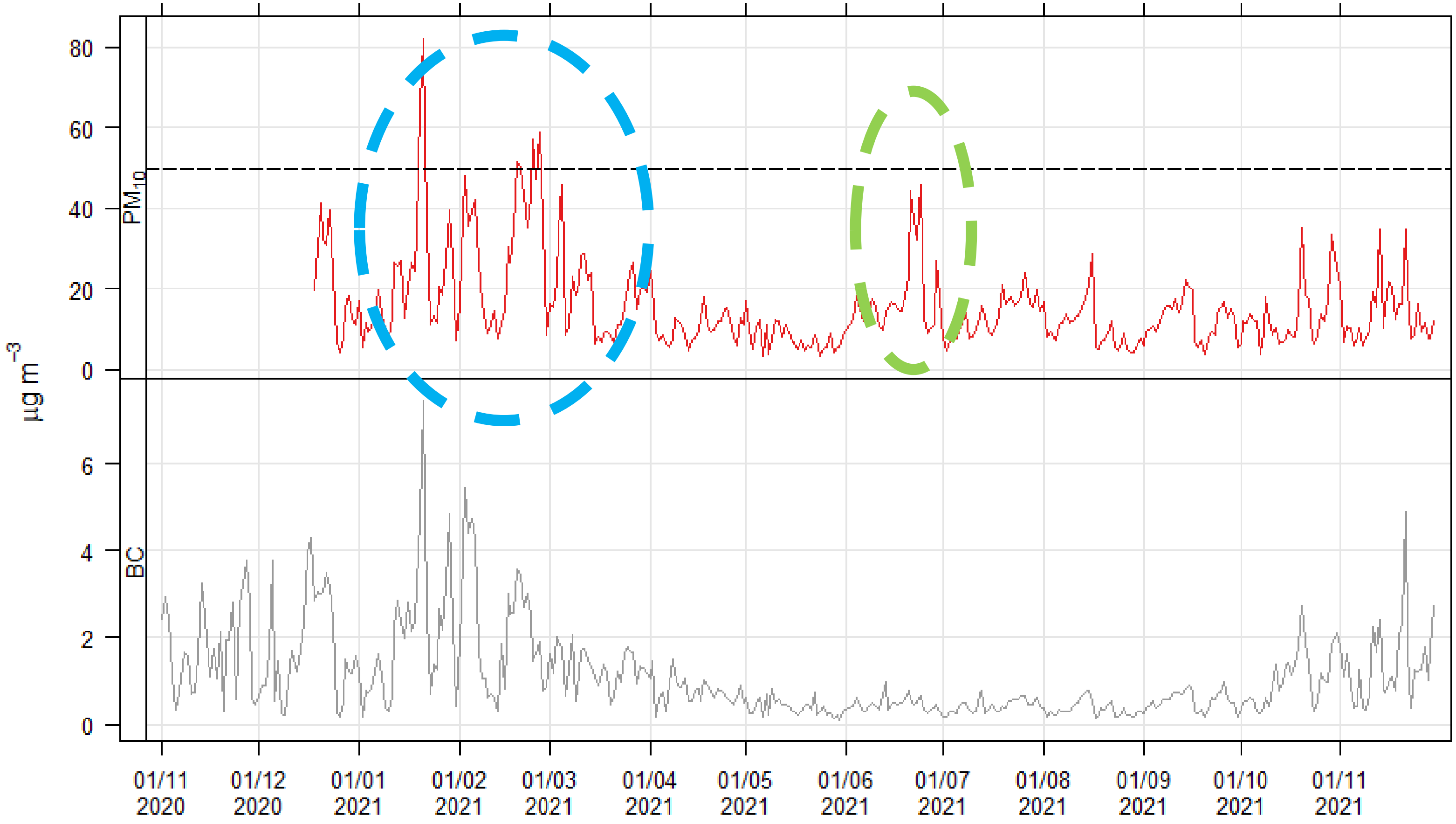
Oxidative potential (OP)

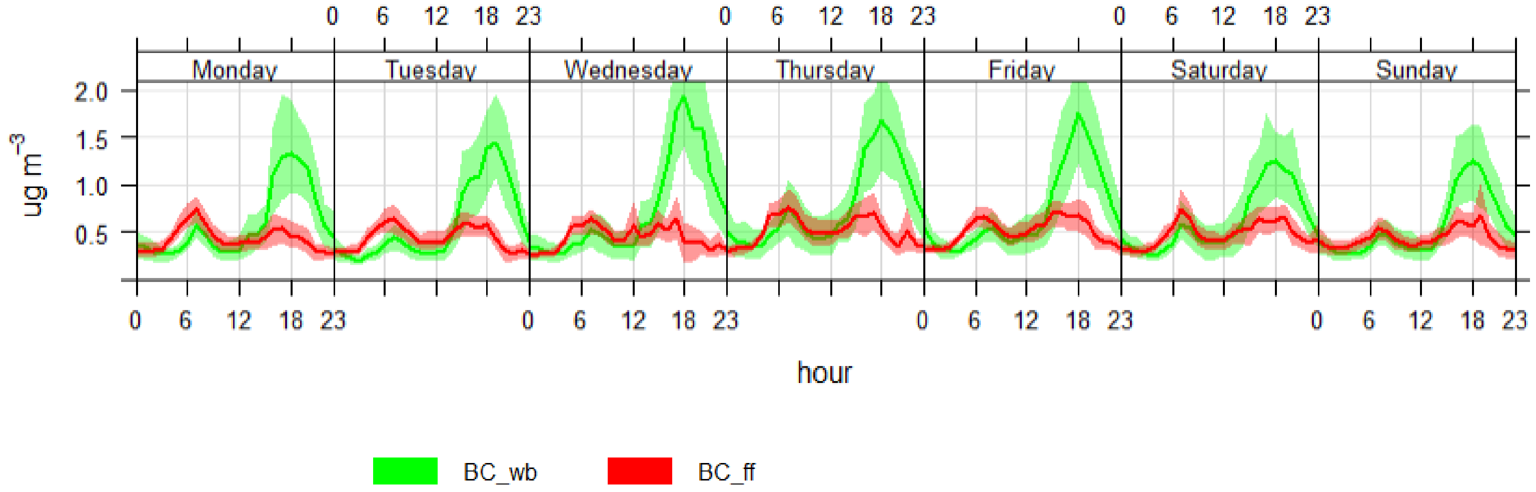


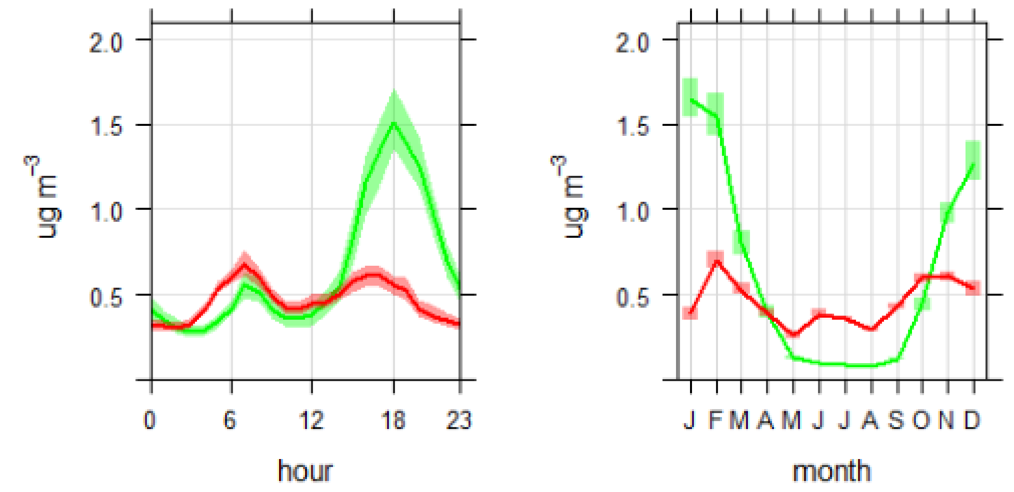
OP^{AA}

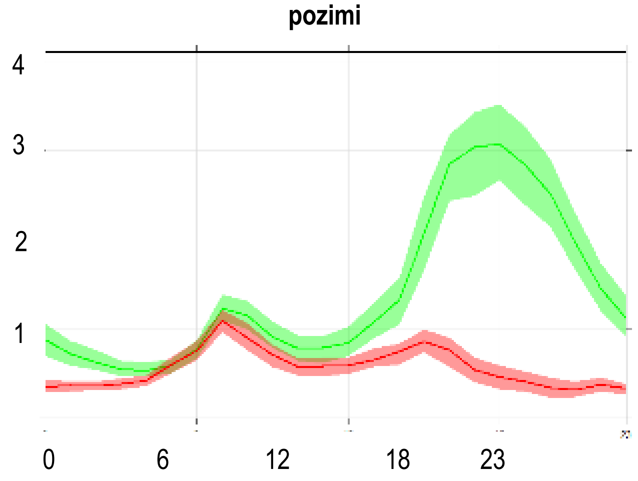
OP^{DTT}

PM_{10}, BC

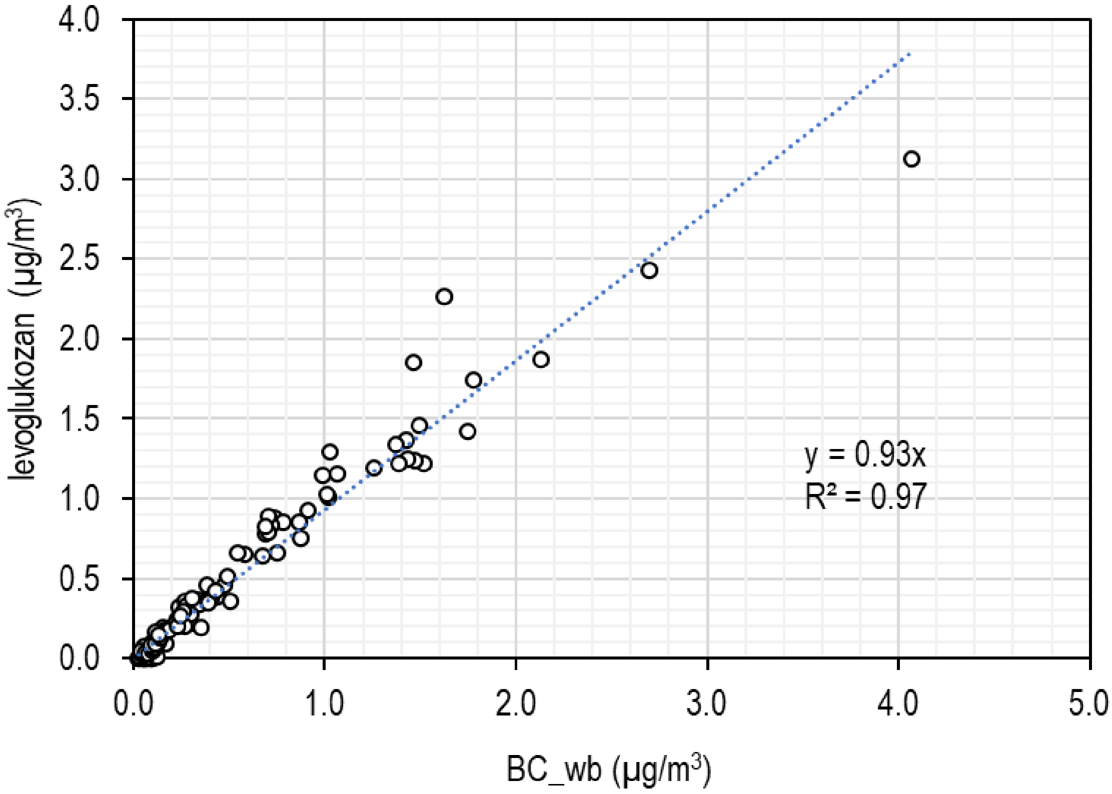

80
60
40
20
0
6
4
2
0
µg m-3
PM10
BC
01/11 2020
01/12 2020
01/01 2021
01/02 2021
01/03 2021
01/04 2021
01/05 2021
01/06 2021
01/07 2021
01/08 2021
01/09 2021
01/10 2021
01/11 2021


Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
ug m-3
hour
BC_wb
BC_ff

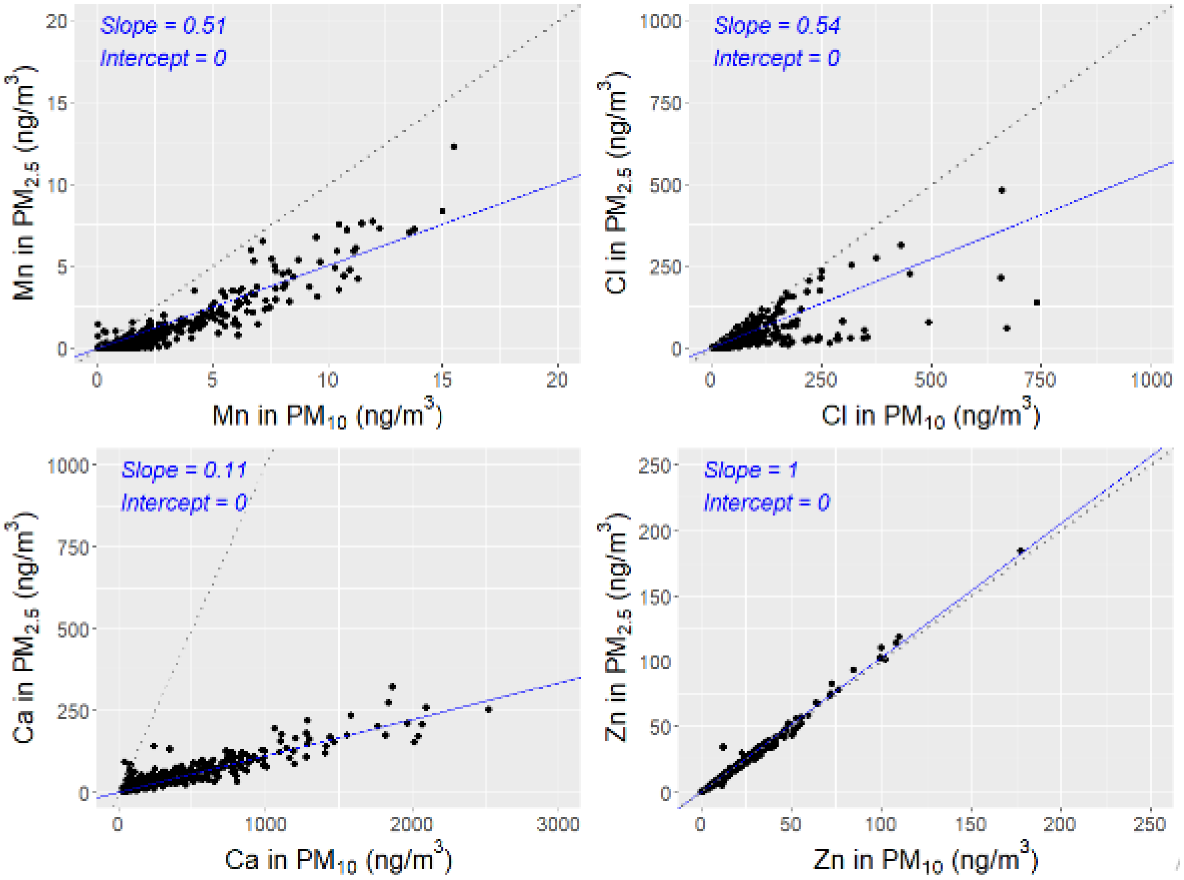

ug m-3
hour
J F M A M J J A S O N D
month

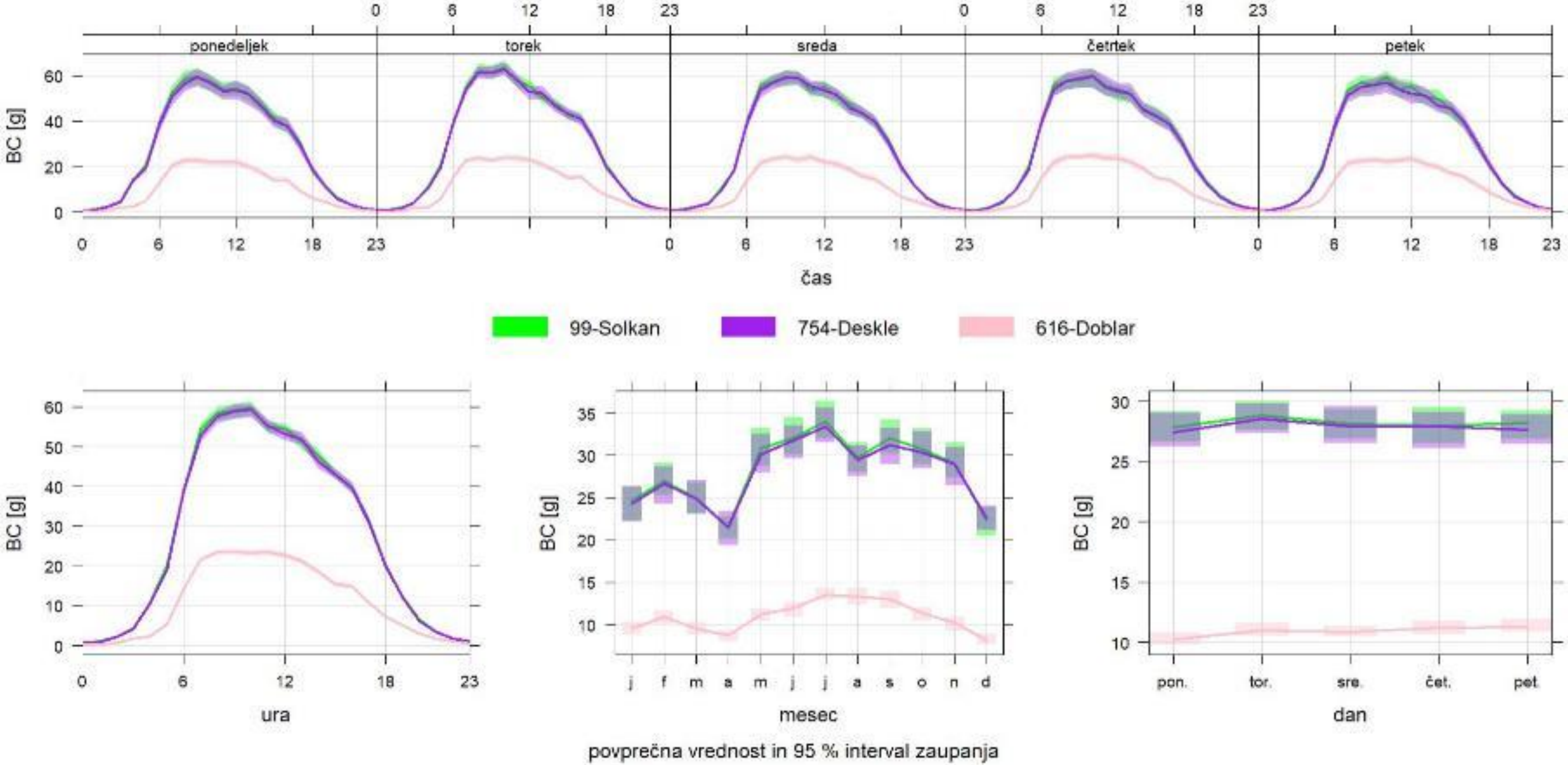

pozimi

eBC and sources



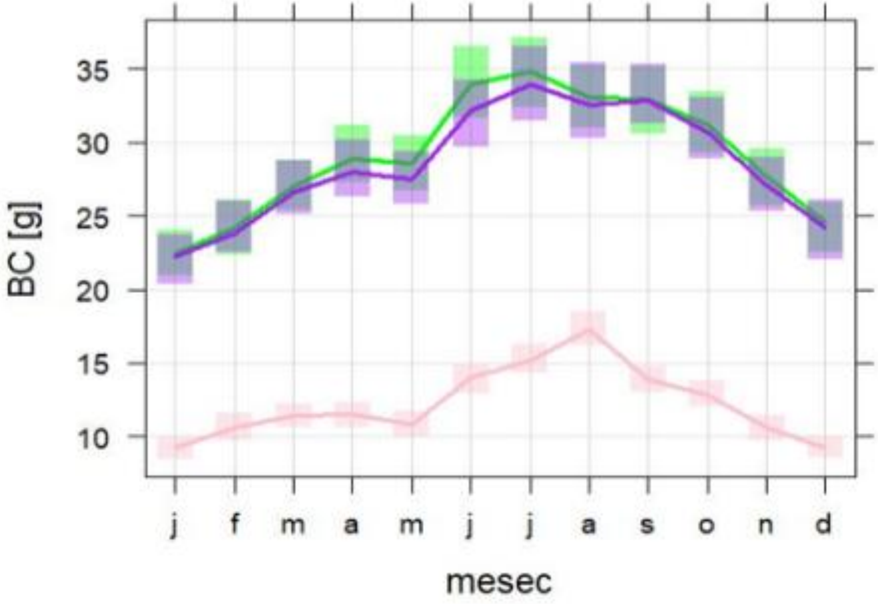
Primerjava kovin fine in grobe frakcije



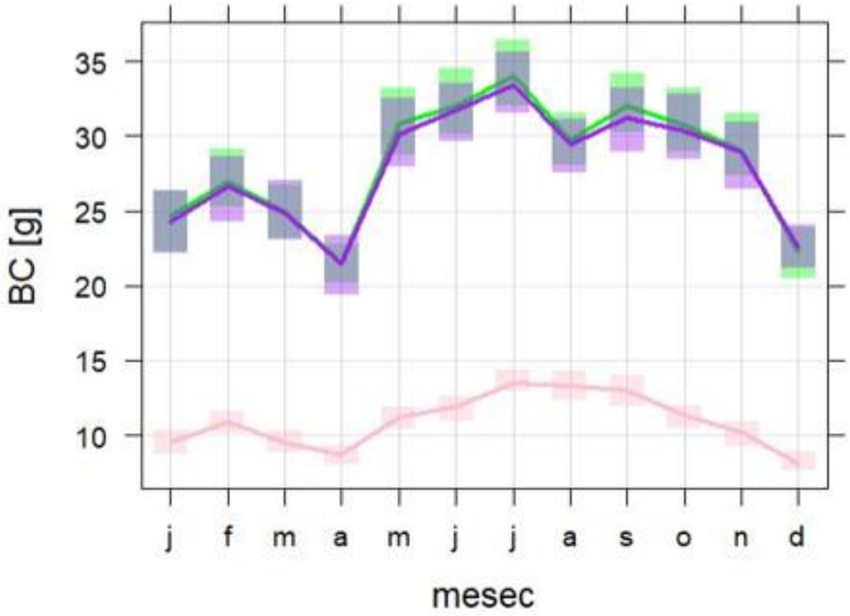


2020
Podkoritnik, 2022

2019

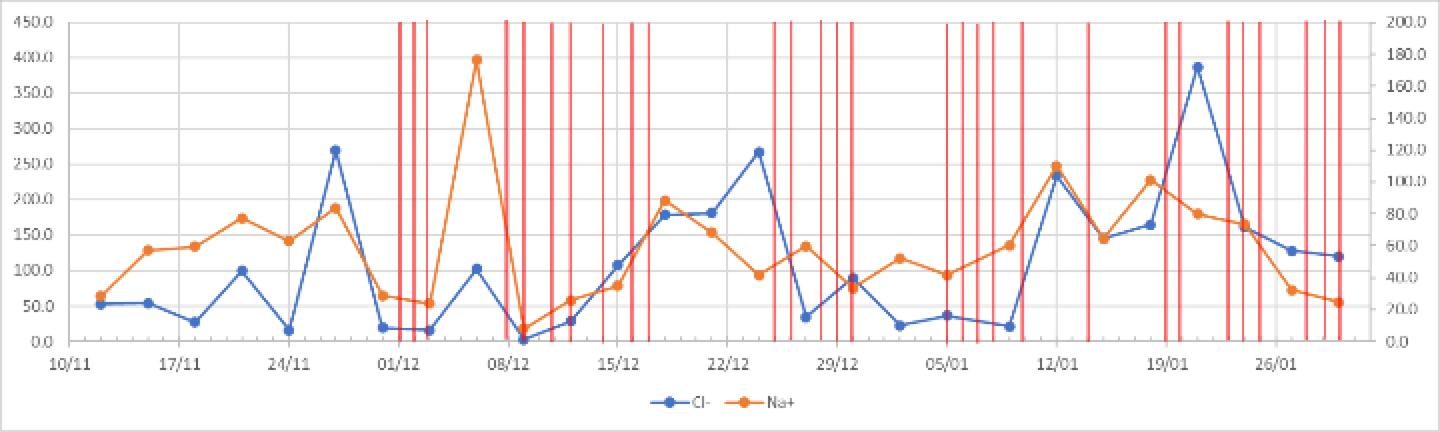


2020



Podkoritnik, 2022

Soljenje cest



PMF formulas

$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$

x_{ij} – concentration of species j measured on sample i

p – the number of factors contributing to the sample

f_{kj} – the concentration of species j in factor profile k

g_{ik} – the relative contribution of factor k to sample I

e_{ij} – the residual of the PMF model for the j^{th} species measured on sample i.

The values of g_{ik} and f_{kj} are adjusted until a minimum value of the objective function Q for a user-selected p is found.

$Q = \sum_{j=1}^{m} \sum_{i=1}^{n} \frac{{e_{ij}}^2}{{s_{ij}}^2}$

s_{ij} – the uncertainty of the j^{th} species concentration in sample I

n – the number of samples

m – the number of species.