# NEW METHODS FOR THE DETERMINATION OF ELEMENTAL COMPOSITION AND SIMPLE PHENOLIC COMPOUNDS IN ATMOSPHERIC PARTICULATE MATTER

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**Doctoral Dissertation**
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**Doctoral Dissertation**

# NOVE METODE ZA DOLOČANJE ELEMENTNE SESTAVE IN ENOSTAVNIH FENOLOV V LEBDEČIH DELCIH OZRAČJA

**Doktorska disertacija**

**Supervisor:** Dr. Martin Šala

**Co-Supervisor:** Dr. Ana Kroflič

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*“Our greatest glory is not in never falling, but in rising every time we fall.”*

*(Confucius)*

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# Abstract

Air pollution is an inevitable problem that modern society has to face today, with particulate matter (PM) being the most dangerous part of it, threatening human health and the environment. Not all PM particles, however, are equally harmful, since the dangerous potential depends on their size and chemical composition, which can vary significantly based on its sources. Anthropogenic emissions, such as traffic, burning of biomass and fossil fuels, and industry are the most problematic sources of atmospheric PM pollution.

To limit PM pollution efficiently, the first step is to identify the most problematic PM constituents and monitor their abundance in the air, which requires accurate and precise analytical methods for their determination. Since PM is a complex mixture of various compounds, research of its whole composition is too extensive to be completed in one project. Therefore, in my dissertation, I focused on the development of two new methods for the determination of important PM constituents: trace elements and simple phenols.

In Europe, four airborne trace elements (As, Cd, Ni, Pb) are regulated (Directives 2004/107/EC and 2008/50/EC) and regularly monitored by a provided standard method (EN14902:2005). This standard method, however, has many drawbacks, mostly originating from the required microwave digestion (MW) pre-treatment. Two of the most important limitations are incomplete PM digestion and production of toxic waste. Therefore, we developed a new method using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), which circumvents the MW digestion step. The developed method is multi-element, accurate, sensitive, fast, and green. Special attention was paid to the examination of sample homogeneity and the related LA sampling protocol, and to the calibration procedure. Apart from a 193 nm LA system used for the method development, a 213 nm LA system was also examined and proposed as a more affordable alternative that could ease the transition to waste-free analytics in air-quality monitoring laboratories. In general, LA-ICPMS was recognized to have the potential of replacing the current standard method in the future, since it is a sustainable method capable of directly analyzing PM collected on the most widely used quartz fiber filters, which is not possible with other surface-based techniques due to the filter thickness or uneven surface.

Airborne simple phenols (*i.e.* phenol, catechol, guaiacol, cresols) are considered toxic, but are not well investigated in PM. Moreover, they can act as precursors to even more harmful nitrophenols. Due to trace concentrations and low ionization efficiency, their determination in PM is difficult, especially without using any sample pre-concentration step, which is commonly accompanied by loss of analytes due to their semi-volatile characteristics. We show that derivatization with dansyl chloride (DnsCl) enables particulate phenols determination with liquid chromatography-tandem mass spectrometry (LC-MS/MS) without the use of a pre-concentration step. Dansylation improved ionization efficiency and the optimized method exhibits good analytical performance, low LODs, and high precision.

Application of the developed methods to ambient PM samples further revealed seasonal trends of target pollutants in Ljubljana, where both trace elements and simple phenols exhibited higher concentrations in colder months compared to the warmer part of the year. This is consistent with the combination of the prevalence of their emission sources and specific meteorological conditions in winter, as are biomass burning for heating purposes and the presence of temperature inversions.

This dissertation provides two analytical methods for trace elements and simple phenols in PM, which show good performance and are consistent with good analytical practices. The atmospheric science community will thus benefit from the alternative multi-element PM determination without concomitant burdening of the environment and by facilitating studies involving particulate phenols, which have been restricted to date.

# Povzetek

Onesnaženje zraka je neizogiben problem, s katerim se sooča sodobna družba, saj so lebdeči delci v ozračju (PM) najnevarnejša komponenta onesnaževanja, ki ogroža zdravje ljudi in okolje. Antropogene emisije, kot so promet, izgorevanje biomase in fosilnih goriv ter industrija, so še vedno najbolj problematični viri onesnaževanja okolja z lebdečimi delci.

Nevarni vpliv, ki ga imajo lebdeči delci na zdravje in okolje, je odvisen od njihove velikosti in kemične sestave, ki se lahko znatno razlikuje glede na vire emisij. Da bi učinkovito omejili onesnaževanje z delci, je treba najprej opredeliti sestavo delcev in spremljati njihovo pojavnost v zraku, za kar potrebujemo točne in natančne analizne metode. Ker je PM kompleksna mešanica različnih spojin, je raziskava celotne sestave preobsežna, da bi jo lahko dokončali v enem projektu, zato sem se v svoji disertaciji osredotočila na razvoj dveh novih metod za določanje pomembnih komponent v PM: elementov v sledovih in enostavnih fenolov.

V Evropi so regulirani štirje problematični elementi v sledovih (As, Cd, Ni, Pb) (direktivi 2004/107/ES in 2008/50/ES), ki jih redno spremljamo z zagotovljeno standardno metodo (EN14902:2005). Ta standardna metoda ima številne pomanjkljivosti, ki večinoma izvirajo iz predpisane predobdelave vzorcev z mikrovalovnim razklopom (MW). Dve glavni pomanjkljivosti sta nepopoln razklop PM različnih sestav in proizvajanje nevarnih odpadkov. Zato smo razvili novo metodo z uporabo laserske ablacije in masne spektrometrije z induktivno sklopljeno plazmo (LA-ICPMS), ki zaobide vse pomanjkljivosti, ki izvirajo iz MW. Med razvojem metode smo posebno pozornost namenili homogenosti vzorca in protokolu vzorčenja z LA ter postopku kalibracije. Razvita metoda je občutljiva, hitra, omogoča večelementno analizo in je prijazna okolju. Za razvoj metode smo uporabili LA 193 nm sistem, kasneje pa smo testirali tudi LA 213 nm sistem kot cenovno ugodnejšo različico, ki bi lahko olajšala prehod na zelene analitske metode, predvsem v laboratorijih, ki redno spremljajo onesnaženost zraka. Ugotovili smo, da bi v bodoče LA-ICPMS metoda (za oba LA sistema) lahko nadomestila trenutno standardno metodo, saj je edina zelena metoda, ki omogoča analizo PM vzorčenega na najširše uporabljenih kvarčnih filtrih, kar je pri drugih površinskih tehnikah problematično zaradi debeline in neravne površine filtra.

Enostavni fenoli (tj. fenol, katehol, gvajakol, kresoli) v ozračju so škodljivi, a v PM niso dobro raziskani, saj je zaradi nizkih koncentracij in odsotnosti funkcionalnih skupin, ki dobro ionizirajo, njihovo določanje težavno, zlasti brez predkoncentriranja. Poleg tega so fenoli v zraku lahko tudi predhodniki mnogo bolj škodljivih nitrofenolov. Dodatni koraki predkoncentriranja lahko povzročijo izgubo analitov, posebno teh s pol-hlapnimi lastnostmi. Pokazali smo, da derivatizacija z danzil kloridom (DnsCl) omogoča določanje fenolov s tekočinsko kromatografijo-masno spektrometrijo (LA-MS) brez predhodnega koncentriranja ekstrakta. Derivatizacija izboljša učinkovitost ionizacije in z optimizacijo instrumentalnih parametrov dosega zelo nizke LODs, zaradi česar smo lahko določili fenole v realnih vzorcih. Razvita metoda je analitično učinkovita, natančna in jo odlikujejo nizke meje zaznave.

Meritve realnih vzorcev so razkrile sezonske trende, pri čemer so bile koncentracije elementov v sledovih in enostavnih fenolov v Ljubljani višje v hladnejših mesecih v primerjavi s toplejšim delom leta, kar je skladno s prevalenco virov emisij, kot je izgorevanje biomase za ogrevanje pozimi, in značilnih meteoroloških pojavov, npr. prisotnost temperaturnih inverzij pozimi.

Ta disertacija ponuja dve novi metodi za določanje elementov v sledovih in enostavnih fenolov v PM, ki ju odlikuje dobra zmogljivost in sta skladni z dobro analitično prakso. Skupnost za raziskave atmosfere je z njima pridobila alternativno večelementno metodo za analizo PM brez dodatnega obremenjevanja okolja in možnost bolj poglobljenih raziskav fenolov v lebdečih delcih ozračja, ki so bile do danes omejene.

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# Abbreviations

| | |
|---|---|
| ACMS | aerosol chemical speciation monitor |
| AMS | aerosol mass spectrometer |
| ANOVA | analysis of variance |
| ARSO | Slovenian Environment Agency<br>(Agencija Republike Slovenije za okolje) |
| BC | black carbon |
| BrC | brown carbon |
| CASS | carbonaceous aerosol speciation system |
| CAT | catechol |
| CMB | chemical mass balance |
| CRE | cresol |
| DnsCl | dansyl chloride |
| EC | elemental carbon |
| EDTA | ethylenediaminetetraacetic acid |
| EDXRF | energy dispersive XRF |
| EEA | European Environment Agency |
| EPA | United States Environmental Protection Agency |
| ESI | electrospray ionization |
| EU | European Union |
| FAAS | flame atomic absorption spectroscopy |
| FIGAERO | filter inlet for gases and aerosols |
| GC | gas chromatography |
| GFAAS | graphite furnace atomic absorption spectroscopy |
| GUA | guaiacol |
| IARC | International Agency for Research on Cancer |
| IC | ion chromatography |
| ICPMS | inductively coupled plasma mass spectrometry |
| ICPOES | inductively coupled plasma optical emission spectrometry |
| INAA | instrumental nuclear activation analysis |
| IPS | International Postgraduate School |
| JSI | Jožef Stefan Institute |
| LA | laser ablation |
| LC | liquid chromatography |
| LIBS | Laser-induced breakdown spectroscopy |
| LOD | limit of detection |
| MARGA | monitoring instrument for aerosol and gasses |
| MS | mass spectrometry |
| MS/MS | tandem mass spectrometry |
| MW | microwave digestion |
| OC | organic carbon |
| PAH | polycyclic aromatic hydrocarbons |

| | |
|---|---|
| PHE | . . . phenol |
| PILS | . . . particle into-liquid sampler |
| PIXE | . . . particle induced X-ray emission |
| PM | . . . particulate matter |
| PMF | . . . positive matrix factorization |
| PTFE | . . . polytetrafluoroethylene |
| SEM-EDXS | . . . scanning electron microscopy coupled with energy dispersive X-ray spectroscopy |
| SMPS | . . . scanning mobility particle sizer |
| SOA | . . . secondary organic aerosol |
| (S)RM | . . . (standard) reference material |
| SRXRF | . . . synchrotron radiation XRF |
| TC | . . . total carbon |
| TD | . . . thermal desorption |
| TOA | . . . thermal optical analysis |
| TXRF | . . . total reflection XRF |
| (U)HPLC | . . . (ultra) high performance liquid chromatography |
| VOC | . . . volatile organic compound |
| WDXRF | . . . wavelength dispersive XRF |
| WHO | . . . World Health Organization |
| XRF | . . . X-ray fluorescence |

# Glossary

**Aerosol** is a multi-phase system of a stable dispersion of solid and/or liquid particles in the gaseous phase (*i.e.* in the air in the context of atmospheric chemistry).

**Particulate matter (PM)** is a part of atmospheric aerosol, denoting only solid, often deliquesced particles from the air.

**Primary organic aerosol (POA)** is atmospheric aerosol consisting of organic particles and gasses, which were directly emitted from a source.

**Secondary organic aerosol (SOA)** is aerosol consisting of organic particles that formed via secondary reactions in the atmosphere (*i.e.* usually particles formed from the oxidation of VOCs).

**Volatile organic compounds (VOC)** are organic compounds in the gaseous state under atmospheric conditions.

**Phenol** – a compound with only single hydroxyl group on a benzene ring.

**Phenols** – a group of compounds containing the phenolic moiety.

**Simple phenols** – for the purpose of the dissertation, simple phenols are defined as phenol and its derivatives containing one other functional group; we focus on those, which could be precursors to SOA (*i.e.* phenol, catechol, guaiacol, cresols).

**Brown carbon (BrC)** is an organic fraction of PM that absorbs solar radiation over a wide range of wavelengths, including in the near-uv and visible regions, typically giving particles brown color. Most commonly, BrC is emitted during biomass and coal burning, or produced in the atmosphere in a form of SOA.

**Acquisition time** is the total amount of time needed for the acquisition of one data point.

**Dwell time** is the amount of time ICPMS uses within acquisition time to measure a specific element.

**Washout time/Single pulse response time** is the time needed to transfer every ablated particle produced by a single shot out of the ablation chamber.

**Fluence** is the energy of laser expressed in J cm$^{-1}$.

**Dosage** is the number of overlapping laser pulses per pixel. In this dissertation, mapping was achieved by measuring lines with continuous movement of the stage, meaning the dosage refers to laser pulses that are partially overlapped. The smear that is produced in this measurement mode is compensated with the drastic improvement in time required for the analysis.

# Chapter 1

# Introduction

Air pollution is an imminent problem that the current society faces today. However, air pollution is not an arising modern issue, since the connection between bad air quality and health was already insinuated in ancient Greece [1]. In later centuries, highly populated areas suffered from the smoke caused mostly due to coal burning facilities. The impaired visibility, depositing soot on buildings and clothing, and damage caused by acid rain were the clear signs of bad air quality, especially after the industrial revolution. The conditions escalated and led to increased mortality during the events with special climate conditions (*e.g.* inversions), trapping air pollutants close to the ground surface (*e.g.* 1930 Meuse Valley, Belgium; 1948 Donora, Pennsylvania; 1952 London, England) [1-3]. These events raised awareness on the importance of good air quality and led to attempts to limit air pollution and regulate toxic emissions by law (*e.g.* Clean Air Act in 1956 was a direct response on the big London smoke in 1952), which eventually improved air quality in big cities of Europe and the United States.

Until nowadays, some major air pollutants have been limited (*e.g.* $SO_2$ from coal burning, lead from petrol) or are decreasing (*e.g.* particle emissions from traffic) [4, 5]. However, 99 % of the world population still lives in places where air quality exceeds World Health Organization's (WHO) guideline limits, which threatens their health and also the environment. The anthropogenic release of gases and particles is still the main cause of excessive amounts of pollutants in the air and is responsible for huge environmental and health problems.

In the European Union (EU), pollutants of major public concern, as are particulate matter (PM), carbon monoxide (CO), ozone ($O_3$), nitrogen dioxide ($NO_2$), nitrogen oxide (NO), sulfur dioxide ($SO_2$), and benzene are regulated and constantly monitored by national environment agencies (EU Directive 2008/50/EC). Among those, PM is classified as the most dangerous air pollutant, which affects more people than any other pollutant, and is often an indicator of air pollution (WHO, 2022). Moreover, due to the complex and variable composition of PM, some of its dangerous components are also regulated and constantly monitored, *i.e.* trace elements: arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb), and benzo(a)pyrene as a marker for polycyclic aromatic hydrocarbons (PAHs) (EU Directives 2004/107/EC and 2008/50/EC).

The constant monitoring of problematic pollutants is necessary to evaluate the success of regulation and new attempts to mitigate air pollution. However, to control and limit air pollution most successfully, governmental regulations and restrictions need to be supported by scientific research and evolve with the advancement in the field. Here analytical chemistry plays an important part in identifying the pollutants and developing new methods for their quantification. For air-quality monitoring purposes, the analytical methods needed for the determination of regulated air pollutants are usually specified by authorities together with the targeted limit values. As the awareness of the dangerous effects of air pollutants increases or their negative effects are identified even at lower concentration levels, stricter regulation is being implemented, needing more sensitive analytical methods with lower detection limits. On the other hand, new pollutants are being recognized as problematic (*e.g.* other trace elements in PM, phenols, nitro-PAHs), which require new robust analytical methods to be implemented in the monitoring process. Furthermore, in the recent years, the development policies recognized the importance of protecting the environment, leading the society towards sustainable future, which should also reflect in analytical laboratories, where a lot of toxic waste is produced, especially during regular analyses as in the air-quality monitoring laboratories. That is why it is important to have and develop new sensitive, accurate, precise, and green analytical methods that can be used in monitoring networks and in the research of atmospheric processes facilitating understanding of atmospheric chemical reactions or emission sources, which are connected with specific marker compounds.

In my PhD, I thus devoted my time to developing new analytical methods for PM characterization; specifically, to develop a more universal and greener method for multiple toxic trace elements (*e.g.* Cd, Pb, Ni, Cr, Zn, etc.) and a new method for simple phenols (*i.e.* phenol (PHE), catechol (CAT), cresols (CREs), guaiacol (GUA)). It is important to note, that, the latter did not exist before. Therefore, in the following chapters I focus on the two specific groups of PM components, which are the main topic of my dissertation: trace elements and phenolic compounds.

## 1.1 PM Pollution and its Negative Effects

PM is classified as one of the most dangerous air pollutants and represents a very diverse group of particles suspended in the air with different compositions, sizes, and shapes, dependent on their sources and lifetime in the atmosphere. PM can be of natural origin, like dust produced by wind erosion of Earth's crust or volcano eruptions, sea spray generated by breaking waves at the sea surface, particles formed by vegetation like pollen, or emissions produced from naturally occurring wildfires. However, emissions due to anthropogenic activities, like PM produced by industry, traffic (including air and sea transport), during fossil fuel and biomass burning for the production of heat, electricity or emitted by agricultural activities, are more problematic. Anthropogenic releases disturb the natural balance and are a source of more concentrated and dangerous PM components (*e.g.* toxic trace elements), which are typically not found in nature. After the particles are released into the atmosphere (*i.e.* primary PM), they can undergo transformations by chemical reactions or physical processes and become secondary PM [6]. In the case of organic particles, the terms primary organic aerosol (POA) and secondary organic aerosol (SOA) are commonly used for describing atmospheric transformations. Apart from releasing PM from different sources, new particles can also form in the atmosphere by gas-to-particle conversion or condensation (secondary PM). Although PM can levitate in the atmosphere for a substantial amount of time (from a day to a few weeks), negatively affecting air quality and influencing climate, it eventually gets deposited on the Earth's surface by dry deposition or is washed out by rain (wet deposition), where it further influences natural and urban ecosystems. PM with longer life-time do not only influence the surroundings of the emission sites, but it can also be transported over long distances and effect more distant places, *e.g.* oceans, wild forests [7, 8].

Since PM is a global pollutant transported by the air, its negative effects are not limited by state borders, so governments should unitedly address the air pollution problem and jointly mitigate most problematic emissions to limit their negative effects.

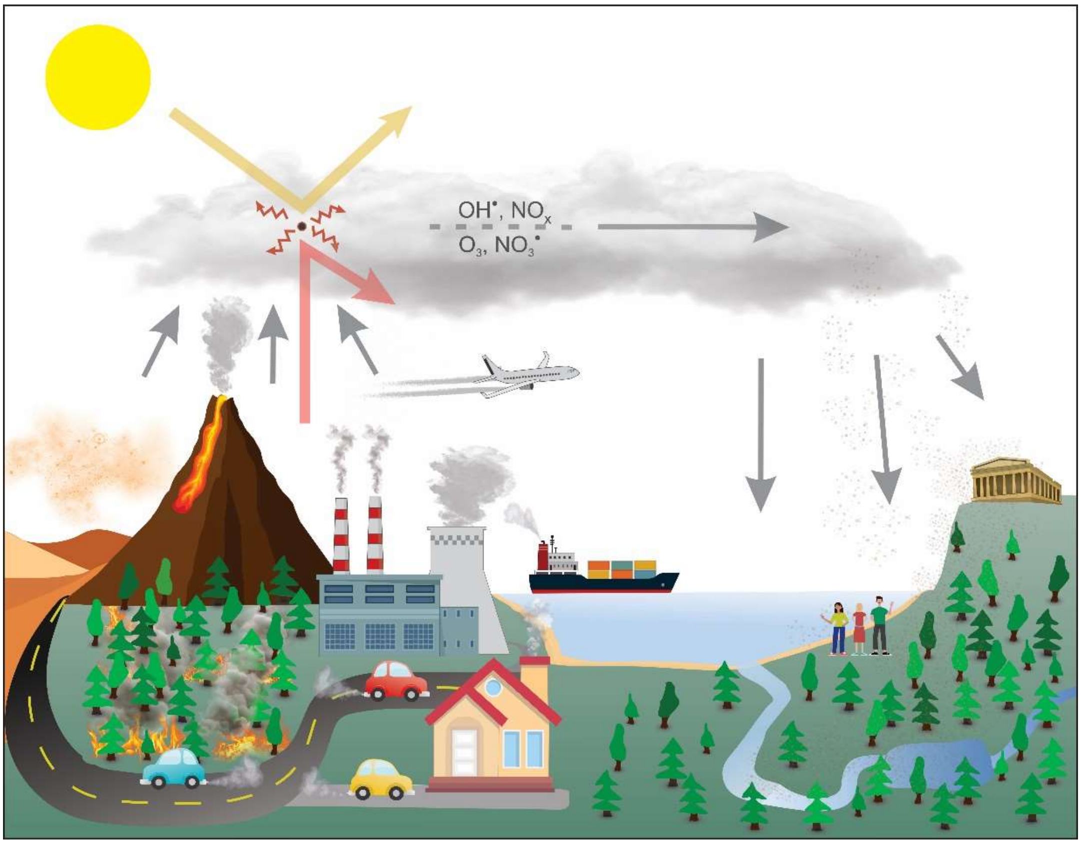


Figure 1: Life-cycle of PM and its deposition pathways: natural and anthropogenic emissions, cloud formation, atmospheric transformations and long-range transport, interaction with terrestrial (red arrow) and solar radiation (yellow arrow), dry and wet deposition impacting remote ecosystems.

### 1.1.1 Air quality and climate

In the atmosphere, PM interferes with the path of sunlight and terrestrial radiation and therefore changes radiative balance and induces climate forcing. The direct influence of PM on climate forcing is by scattering and absorbing the light, overall causing cooling of the Earth (by releasing less sunlight to Earth's surface) and warming of the atmosphere (by absorbing some part of radiation energy and backscattering the radiation from the Earth) [8]. The PM components with the highest light-absorbing impacts are (i) black carbon (BC), a sooty black material with the highest absorption efficiency in the UV-vis wavelength range, often equalized with elemental carbon (EC) and produced by incomplete combustion of carbonaceous fuels; (ii) brown carbon (BrC), a group of organic aerosols absorbing in a wide wavelength range (including near UV (300–400 nm) and visible regions), and observed as yellowish-to-brown colored aerosols with high light scattering abilities, most often a result of biomass burning and secondary transformations in the polluted atmosphere; and (iii) mineral dust, mostly derived from natural sources, *e.g.* Saharan dust [9]. Some simple phenols, such as *m*- or *o*-CRE absorb in the range of BrC, whereas those absorbing characteristics are even potentiated when transformed into specific secondary derivatives in the air, as are phenols containing additional nitro-group on the benzene ring (nitrophenols). Nitrophenols are known for their strong light absorbance and belong to a group of BrC components, which are known to affect climate forcing [10]. Trace elements, on the other hand, represent a small part of PM, so their influence on climate is usually not separately studied [11].

PM can also serve as nuclei for water vapor condensation and the formation of clouds or ice particles. The PM composition thus further defines microphysics, radiative properties and lifetime of clouds and so affects climate forcing also indirectly [12]. For example, in more polluted atmosphere, clouds with more and smaller droplets are formed, reflecting more solar irradiation compared to cleaner atmospheres [8].

Apart from the disturbed radiative balance, high PM concentrations reduce visibility, which is especially pronounced in large cities, damaging the appearance of the surrounding [13], and causing negative effects on people's mood [14] and some economy sectors, such as tourism [15].

### 1.1.2 Ecosystem

The ecosystem is influenced by PM pollution at many different levels. As already implied, PM interacts with sunlight and affects the ecosystem indirectly by changing the air temperature and the amount of sunlight received. Moreover, PM also affects the ecosystem directly, by inhalation and/or deposition on plant leaves, soil, groundwater, *etc.*, where toxic compounds in PM can exert additional harm. PM pollutants enter plant tissues through foliar or root uptake. Entering of metals was confirmed through both pathways [16, 17], while for phenols (GUA, 4-nitroguaiacol), studies only for root uptake [18] have been conducted so far. PM can also deposit on soil, where it disturbs soil chemistry and affects nutrient cycling or can even be leached to groundwater. This can result in reduced growth and biodiversity of vegetation and microbiota [19]. For instance, the decomposition rate was shown to be affected in oak leaves containing heavy metals (Fe, Zn, Cu, Cr, Ni, Pb), probably due to disturbed microbial balance or its metabolic activity [17]. The effect of PM pollution on forests was observed in some heavily polluted areas. In the northeastern United States, forest decline has been correlated with the deposition pattern of heavy metals [17] and in Italy, an increased concentration of nitrophenols in leaves was found at the damaged forest site [20]. Furthermore, persistent PM components, especially the ones of poor water solubility, get mixed with soil and even accumulate in some plants, and so they can enter the food chain [19]. For example, near the zinc smelter, cadmium levels in deer's internal organs were five-times higher than at more distant places [17], which could be the result of the polluted feed or air. The effects of atmospheric pollution on the ecosystem, however, are difficult to investigate since they can sometimes pop up only after 10 or more years of accumulation [17].

In the open ocean, the deposition of atmospheric aerosols is an important source of nutrients and trace metals to the ocean, so the anthropogenically changed composition of PM can importantly influence the marine biota [21]. Some types of aerosols can enhance the growth of particular phytoplankton species, while others, allegedly aerosols containing copper, have a toxic effect on the phytoplankton [22]. Aquatic organisms [23-25] and marine bacteria [26] can also be negatively affected by phenols especially their nitrated derivatives.

### 1.1.3 Immovable cultural heritage

The impact of PM pollution has also been found detrimental in the anthroposphere. One example is cultural heritage, where historical buildings and outdoor art sculptures are constantly exposed to PM deposition. The PM influences the materials by soiling (deposition of exogenous particles on the surface) and formation of black crusts (*i.e.*

sulfation process accompanied by PM deposition), which damage material surfaces or even influence the stability of the structures. Trace elements from PM present in the deposited layers have been used for identification of past pollution sources responsible for the appearance of black crusts and soiling, where historical buildings act as natural passive samplers for PM pollution [27]. Based on trace elements fingerprint, the sources such as coal burning, mostly present from extensive use in the previous century, and traffic as a prevalent source today have been identified [28]. Furthermore, PM was shown to play a critical role in the black crust formation process (calcium carbonate is transformed to more soluble calcium sulfate dihydrate (gypsum) in the presence of atmospheric $SO_2$ and humidity), as metallic particles are involved in the catalytic oxidation of $SO_2$ [11, 29]. Rodriguez-Navarro and Sebastian [30] reported that diesel engine exhaust containing large quantities of soot, Fe, Fe-S, Cr, Ni, Cu, and Mn have higher fixation rate of $SO_2$ than gasoline engine exhausts containing a smaller amount of soot and a larger amount of Pb and Br.

The composition of soiling material reflects the abundance and composition of PM in ambient air. Although nowadays traffic is a prevailing source of PM in urban areas, the organic carbon (OC) is expected to be the main soiling component in the future. However, the composition of the organic fraction of PM is still poorly characterized, including phenolic content, therefore its influence on deposited surfaces is difficult to predict and still needs to be investigated [31].

### 1.1.4 Health

PM is one of the leading health risk factors, 6th on the list (project of the Institute for Health Metrics and Evaluation), right after high blood pressure, blood sugar, body weight, smoking and children undernutrition [32]. It is estimated that in 2019, 4.14 million premature deaths worldwide were linked to ambient $PM_{2.5}$ pollution, which is 62 % of all air pollution-attributed deaths (State of global air, 2022). Diseases such as heart disease, stroke, chronic obstructive pulmonary disease, lung cancer and acute respiratory infections are all connected to PM pollution [33, 34]. The cut-off size of PM, which can enter the upper respiratory tract and is associated with health risk is less than 10 µm in diameter ($PM_{10}$), and according to some studies [35, 36] particles smaller than 2.5 µm ($PM_{2.5}$) are the most dangerous. The smallest PM particles can penetrate deep into the lungs and enter the blood system, causing lung and cardiovascular diseases, and ultrafine particles (particles smaller than 100 nm) can even enter the brain through olfactory system or penetrate through the blood-brain barrier [37-39]. In 2013, WHO classified air pollution as a possible cause of lung cancer [40] and the International Agency for Research on Cancer (IARC) announced that PM is one fraction of air pollution that is considered carcinogenic to humans [41].

Beside the PM as a whole, which is known to promote the generation of reactive oxygen species in lung tissue, particular PM components are further associated with specific adverse effects on human health. While a few trace metals and simple phenols found in PM are known (As, Cd, Cr, Be, Ni) [40] or classified as possible human carcinogens (cresols, catechol) (United States Environmental Protection Agency (EPA), International Agency for Research on Cancer (IARC)), phenol, catechol, and cresol are also put on the list of Hazardous Air Pollutants issued by EPA (EPA, 2005). Some of the observed adverse effects on body organs by toxic elements were the impaired function of kidneys (Cd, Pb, Ni, Hg), respiratory system (Cd, Ni, Hg), reproductive system (As, Pb, Hg), liver (Pb), and skeletal system (Cd) [42]. Similarly, the exposure to phenols exhibited adverse outcomes like respiratory tract irritation and studies on animal models revealed that long-term exposure to phenol and cresols can affect blood, liver, kidney, central nervous system, and cause body weight loss, small hemorrhages in the lungs, degradation of heart muscle, and reduced locomotor activity (EPA, WHO). On a cell level, some elements and phenols (Fe, V, Ni, Cr, Cu, Zn, catechol) are also generators of reactive oxygen species, causing dangerous oxidative stress in biological tissues [43]. Some components, such as catechol, can even form DNA adducts or complexes with multivalent ions, *e.g.* Fe, Cu, which can produce DNA damage [44]. Furthermore, phenolic derivatives, which could be secondarily formed from simple phenols in the atmosphere (*i.e.* nitrophenols, methylnitrophenols), can act as endocrine-disrupting compounds [45-49].

Related to the recent events, PM pollution can also worsen the course of other diseases, *e.g.* Covid-19. The Covid-19 mortality rate in China was increased because of PM pollution [50]. In the United States, it was estimated that an increase of 1 $\mu g\ m^{-3}$ in PM$_{2.5}$ concentration is associated with an 8 % increase in Covid-19 death rate [51].

### 1.1.5 PM size and chemical composition

The size of airborne particles can be defined in two different ways: (i) by an index to PM (*i.e.*, PMx, where x means the maximum size of particles in a fraction in µm) or (ii) descriptively, where slightly different size ranges are used depending on the author. Typical size fractions of PM are described in Table 1. Most commonly measured PM fractions are PM$_{10}$, denoting particles small enough to influence the human health and light enough to hover in the air for long periods of time and allowing to travel long-distances, and the smaller PM$_{2.5}$ fraction, which is small enough to enter the bloodstream through the lungs and cause severe health effects (EPA, European Environment Agency (EEA)) [42, 52].

Table 1: Size fractions of PM.

| **Designation by index** | **Size (µm in diameter)** |
|---|---|
| PM$_{10}$ | $< 10$ |
| PM$_{2.5}$ | $< 2.5$ |
| PM$_{1}$ | $< 1$ |
| PM$_{0.1}$ | $< 0.1$ |
| **Descriptive designation** | |
| Total suspended PM (TSP) | $< 35^{a}$; $<50$–$100^{b}$; $< 25$–$45^{c}$ |
| Coarse PM | $> 1$–$3^{a}$; PM$_{10}^{b}$; 2.5–$10^{c,d}$; $> 2^{e}$ |
| Fine PM | $< 1$–$3^{a}$; PM$_{2.5}^{b,f}$ |
| Accumulation mode | 0.1–$2^{a,e}$ |
| Ultrafine PM | $< 0.1^{a}$ |
| Nuclei mode | 0.005–$0.100^{a,e}$ |

[a]Turner and Colbeck [6], [b]EEA, [c]EPA, [d]Chen, et al. [2], [e]John [53], [f]EU directives (EU) 2016/2284 and 2008/50/EC)

However, negative effects of PM are not solely due to particle size, but are largely connected to their composition as well. Typical components of PM are inorganic (*i.e.* EC, crustal elements, ions, and trace elements) and organic compounds (mostly denoted with the OC fraction, which includes phenolic compounds). Among these, particular trace elements and phenols are toxic to humans and harmful to the environment (see previous chapter).

The size and composition of PM is defined by its sources, time spent in the atmosphere, and weather conditions. The dynamic processes in the air, such as coagulation or molecular transfer between the particle and the surrounding gas (*e.g.* condensation, evaporation, nucleation, adsorption, absorption, and chemical reactions), are constantly changing the size and composition of PM [54]. Although a lot of research exists studying processes in the atmosphere, either by laboratory, atmospheric chamber studies, modeling, or field studies, many of these processes are still not understood [55, 56].

#### 1.1.5.1 Source apportionment

However, the size and chemical composition of PM alone do not provide sufficient information for targeted restrictions that allow for the efficient mitigation of air pollution. Instead, emission sources need to be identified based on the acquired data. This is achieved by applying source apportionment analysis, which is a statistical procedure of identifying major emission sources and their shares in airborne pollution, based on analyte concentrations measured in ambient samples.

The most commonly used source apportionment methods for PM use receptor models, such as positive matrix factorization (PMF) and chemical mass balance (CMB) [57]. In receptor models, the measured analyte mass at a given site is attributed to different sources by solving a mass balance equation (1). The assumptions that need to be accepted when working with receptor models are: i) source profiles are constant over time and ii) chemical species included in the model do not react with each other or undergo phase partitioning when they are transported from the sources to the sampling site [58]. The type of chemical species included in the model depends on the studied area, the object of research, and the available analytical instrumentation. The possible input data can include species like ions, carbonaceous fractions, elements, organic markers, mass fragment (*m/z*) concentrations, and isotopic ratios, as well as physical properties like aerosol size distribution and optical properties. The species included should provide information specific for different sources, *e.g.* elemental tracers (Table 2) are often crucial for identifying pollution sources. Organic molecular markers, on the other hand, are much less investigated, but some of them, for example methoxyphenols, syringol, and levoglucosan have been identified as good markers of biomass burning [57-61]. In order to avoid false interpretation of receptor model results, it is important to be familiar with the background of the area surrounding the receptor site, major emission sources, possible point sources and their spatial distributions, and topography (*e.g.* mountains, valley terrain, tall buildings, water bodies, wind directions), which influences air transport to/from the receptor site.

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

$X_{ij}$..........concentration of j-th species in the i-th sample
j.............species
i.............sample
$g_{ik}$..........contribution of the p-th source to the i-th sample
$f_{kj}$...........concentration of the j-th species in the p-th source
$e_{ij}$...........uncertainty term

The CMB model is based on the effective-variance least-square approach. The required input data are concentrations of measured species, their uncertainties and the fingerprints/profiles of local sources with their uncertainties. It is an ideal model for analyzing small datasets, since the model can be solved even with just one sample. However, in practice, more samples are usually used for better confidence. The limitation of the model is the required pre-determined information on local source profiles, which are not always available. When using a source profile from the existing database (*e.g.*

SPECIATE, SPECIEUROPE), specific properties of the studied area should be considered (*e.g.* harbor, surrounding industries, wood or coal burning). If the solutions given by the CMB model do not agree with the desired goodness-to-fit parameters (R-square, chi-square, and species' calculated-to-measured ratios), probably some assumptions are incorrect. In that case, source profiles could be non-representative for the selected area or there were some missing source profiles [57].

On the other hand, the PMF model is based on uncertainty-weighed factor analysis, with restrictions to provide non-negative source contributions. The input data for this model does not require predefined source profiles, but only the number of sources, together with species concentrations and uncertainties for each parameter. The PMF model requires more samples than CMB; roughly at least 3-times higher number of samples is needed compared to the number of variables [57]. However, in practice, the number of samples cannot be simply determined; the population of samples has to contain enough variability with different relative contributions of the sources. Based on the input data, the model generates source profiles and provides information on species contribution and uncertainties [62]. The analysis is usually performed several times, with different numbers of contributing factors and the optimal solution is chosen by examining output model characteristics (*e.g.* Q-values, scaled residuals, regression parameters, species/mass reconstruction) [57]. The most commonly determined factors are sea/road salt, crustal/mineral dust, traffic, secondary inorganic aerosol, and biomass burning.

#### 1.1.5.2 Elemental composition

PM mostly consists of a plethora of carbonaceous components, ions, and oxides from soil, which makes carbon (C) and other elements constituting organic compounds (O, H), and ions (N, S) the most abundant elements in PM. However, when talking about the elemental composition of PM, focus is on trace elements, although they contribute very little to the total PM mass (in six EU cities, the contribution of other elements was estimated in the range of 0.3–1.8 % [63]); however, the related negative influences on human health and the ecosystem are not irrelevant (see Section 1.1).

Trace elements can be emitted from natural sources, as are minerals from soil erosion, volcano eruptions, sea-spray, and naturally occurring fires (*e.g.* Fe, Al, K, Na, Cl, Ca, Mg, Si; those "macro" elements are usually present in higher proportions), or they can be emitted from anthropogenic sources like traffic, industry, mining, coal burning and other heating-related processes (*e.g.* Pb, Cd, Ni, As, Sb, Zn, V, Cu, Cr; "micro" elements are usually found in trace amounts). Some trace elements are specific for the source type and are therefore good markers for source apportion studies. For example, the following elements are markers for traffic (Ba, Cu, Fe, Pb, Zn), motor oil (Cu), tire wear (Cu, Mn), break wear (Ba, Cu, Fe, Mn, Mo, Sb, Sn, Zn), fossil fuel (Ni, S, V), coal combustion (As, Cl, Co, Sc, Se), residual oil combustion/ship emissions (Ni, V), metallurgic industries (Cu, Fe, Mn, Zn), non-metallurgic industries (As, Cr, Cs, Mo, Ni, Pb, Tl, Zn, Zr), wood burning (K, together with levoglucosan), sea spray or salting of roads in winter (Cl, Mg, Na), and crustal/mineral dust (Al, Ca, Fe, Mg, Mn, Si) [58, 59, 64-66]. Not all marker compounds are necessarily universal. Some can be specific for the location, other represent sources, or specific materials used. For example, in SPECIEEUROPE data base, 37 biomass burning and 66 traffic source profiles are recorded. Elemental tracers/markers used for the identification of sources by the Slovenian Environment Agency (ARSO) are presented in Table 2.

Table 2: Elemental tracers/markers for emission sources.

| **Sector** | **Source** | **Tracer/Marker** |
|---|---|---|
| Traffic | Traffic emission | Br, Pb, Ba, EC, Mn, Cl, Zn, V, Ni, Se, Sb, As, PAH |
| | Tire wear | Zn |
| | Break wear | Cu, Zn, Pb |
| | Dust from traffic | EC, Al, Si, K, Ca, Ti, Fe, Zn |
| Industry | The industry of iron and steel | Pb |
| | Refinery | V |
| | Cement factory | Mg, Al, K, Tl, Mn, Fe |
| Domestic emissions | Wood burning (domestic or natural fires) | Levoglucosan, PAH, EC, Ca, Na, K, Fe, Br, Cl, Cu, Zn |
| | Coal burning | Se, As, OC, EC, Cr, Co, Cu, As, S, P, Ga |
| | Fuel oil | EC, V, Ni |
| Natural sources | Sea-spray aerosol | Na, Cl, S, K |
| | Resuspension | Si, V, Cr, Ca, Ti, Sr, Al, Mn, Sc |
| | Mineral dust | Si, Al, Ca, Mg |
| Secondary particles | Agriculture | $NH_3$ |
| | Coal, foundry, ships | $SO_2$ |
| | Combustion | $NO_x$ |

Source: ARSO, 2013 [64]

In the EU, four elements (*i.e.* As, Cd, Ni, Pb) are recognized as toxic for humans and their concentration in PM is regulated (limit values are prescribed) and constantly monitored. Their most common sources in EU countries are presented in Figure 2, with industry and energy supply sectors being the largest contributors to any of them. Transport also contributes substantially to Ni (non-road transport as air, rail, sea and inland water transport) and Pb emissions (road transport), and residential, commercial and institutional sources contribute especially to Cd and Ni. Waste sector (waste water management) contributes significantly to As.

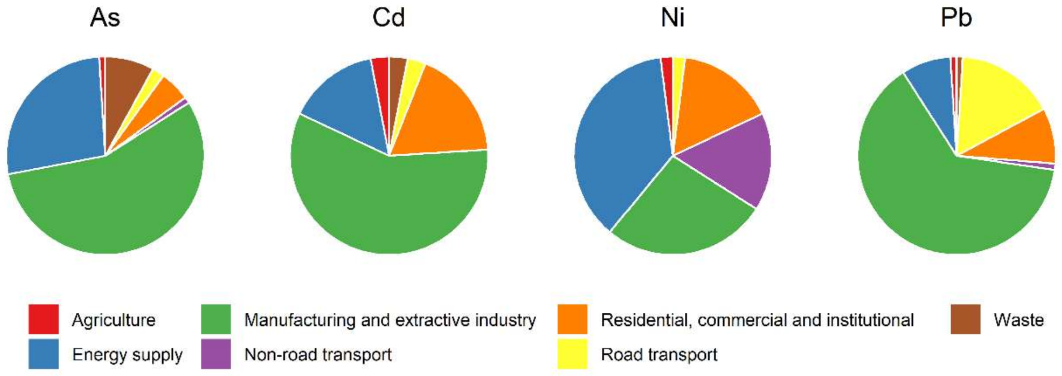


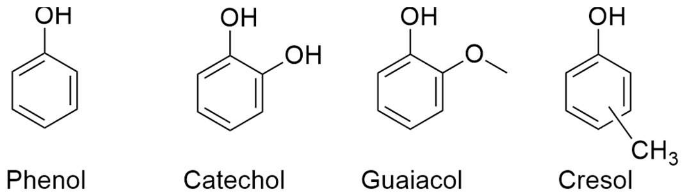
Figure 2: Emission sources for As, Cd, Ni, and Pb in EU (2018). Source: EEA, 2020 [19].

#### 1.1.5.3 Particulate phenols

Phenols are mostly emitted during anthropogenic activities, such as biomass burning (products of lignin thermal degradation), traffic, and fossil fuel combustion [67, 68]. The majority of simple phenols of our interest (*i.e.* PHE, CAT, GUA, CREs; Scheme 1) are produced by primary emissions. Due to their relatively high volatility and fair water solubility, they are bound to particles or present in the atmospheric gas. Campen, et al. [69] showed that in diesel exhaust, both phases (PM and gas) contribute to its toxicity; therefore, even though simple phenols are most commonly considered gaseous pollutants, their contribution to particulate fraction should also be investigated.

Although simple phenols are toxic by themselves, their effect on the environment is even enhanced when they act as precursors to secondary phenols, which are formed by *e.g.* nitration or oxidation in the atmosphere. The most abundant reactive species promoting atmospheric transformations are hydroxy radicals ($OH^\bullet$), nitrate radical ($NO_3^\bullet$) ozone ($O_3$), nitrogen oxides ($NO_x$), and nitrous acid (HONO), in the presence or absence of sunlight (*hv*). Oxidation mediated by $OH^\bullet$ can transform PHE, *o*-CRE, *p*-CRE, and GUA to CAT, 3-methylcatechol (3MC), 4-methylcatechol (4MC), and 3-methoxycatechol, respectfully [70]. Moreover, nitration with $NO_3^\bullet$, HONO and $NO_x$ in the presence of $OH^\bullet$ can change: (i) CAT to 4-nitrocatechol (4NC), (ii) 3MC to 3-methyl-4-nitrocatechol (3M4NC), 3-methyl-5-nitrocatechol (3M5NC), or 3-methyl-6-nitrocatechol (3M6NC), (iii) 4MC to 4-methyl-5-nitrocatechol (4M5NC), and (iv) GUA to 4-nitroguaiacol (4NG) or 6-nitroguaiacol (6-NG) [71-76]. Other authors further observed the formation of aromatic SOA with brown carbon properties from the reactions of CAT and GUA with $O_3$ or $NO_3^\bullet$ [71, 77]. Nitrophenols are more toxic than their precursors, and usually more stable in the atmosphere, prolonging their negative impacts on the climate and human health. Some phenolic derivatives were even recognized as so source-specific that they were characterized as molecular markers for biomass burning (*i.e.* methoxyphenols and methylnitrocatechols: 4M5NC, 3M5NC, 3M6NC)[57, 76, 78-81].

Seasonal variation of particulate simple phenols was only investigated in one study so far [82], probably due to the lack of appropriate analytical methods. The highest concentrations of phenolic precursors were observed in winter and the lowest in summer, which was expected due to additional biomass burning sources in winter [82]. Similarly, in studies involving nitrophenols, which are closely connected with their precursor simple phenols, the highest concentrations were observed in winter, when biomass and fossil fuels are extensively used for heating purposes. The lowest concentrations were typically measured in spring and summer. In Ljubljana, the highest proportion of nitroaromatic components was attributed to nitrocatechols (alkyl nitrocatechols and 4-nitrocatechol) in all seasons. In summer, nitrosalicylic acids and nitrophenols also contributed quite substantially, and in winter, 4-nitrosyringol and nitroguaiacols could also be detected [83]. Simple phenols have not been determined in Ljubljana so far. Although some relations between simple phenols as precursors and nitrophenols as secondary derivatives have been confirmed under laboratory conditions, condensed-phase transformation processes are still poorly understood and need to be investigated further, including in real-life conditions.



Scheme 1: Simple phenols investigated in the dissertation. The methyl group in cresol can be placed at *orto*- (*o*-CRE), *meta*- (*m*-CRE) or *para* (*p*-CRE) positions.

## 1.2 Air Quality Monitoring

PM pollution has negative consequences all over the world. To assure safe living conditions and limit the influence on the climate, it is important to constantly monitor pollutant levels in the air and act accordingly. Ideally, a well-positioned monitoring network or targeted campaigns provide information that allow for:

(i) assessing the living conditions regarding the quality of air, so that additional restrictive measures can be applied to limit air pollution if conditions are not adequate (*e.g.* Air quality index) [84],
(ii) identifying emission sources, so that restrictions can directly target identified sources of pollution [57],
(iii) evaluating the success of restrictive measures, by tracking negative trends of pollutants,
(iv) studying the influence of long-range transport of pollutants, which can spread negative influence far from emission sources,
(v) building (long-term) model predictions of pollutant levels and their impacts in the future, and
(vi) building (short-term) model predictions of events of severe air deterioration (*e.g.* high PM concentrations or SOA formation) and forecasting local air quality, so that additional restrictions (*e.g.* limiting coal burning facilities or traffic) or warnings can be released (*i.e.* to avoid outside air/activities if possible, especially for sensitive groups of people as children, elderly, asthmatics and other pulmonary-compromised patients) [85].

Therefore, many regulatory organs instruct air quality monitoring and limit major toxic pollutants, as are ozone ($O_3$), carbon monoxide (CO), nitrogen oxides ($NO_x$), sulphur dioxide ($SO_2$), and PM (WHO, EEA, EPA); in EU, benzene and volatile organic compounds (VOCs) are also included. Along with measuring mass concentrations of $PM_{10}$ and $PM_{2.5}$ fractions of atmospheric aerosols, European parliament and the council also require the determination of PM chemical composition, targeting trace elements (*i.e.* As, Cd, Ni, Pb, Directives 2004/107/EC and 2008/50/EC), water-soluble ions (*i.e.* $SO_4^{2-}$, $NO_3^-$, $Na^+$, $K^+$, $NH_4^+$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$), PAH, EC, and OC. The limit values for PM and trace elements set in EU and guidelines recommended by WHO are listed in Table 3.

To assure comparable results in all member states, EU further provided a standard method for the determination of the regulated analytes (for trace elements see details in Section 1.3.2.1). Furthermore, to improve air quality in EU, reduction of major pollutants (*i.e.* $PM_{2.5}$, $NH_3$, $SO_2$, $NO_x$ and non-methane volatile organic compounds) has been prescribed until 2029 and from 2030 onwards. Moreover, monitoring of additional trace elements (*i.e.* Cr, Cu, Se, Zn) is also required (Directive (EU) 2016/2284), even though the standard method is not optimized for those elements (drawbacks listed in 1.3.2.1).

Table 3: Limit values by EU and WHO guidelines for PM and elemental concentrations in the air.

| **Pollutant** | **Averaging period** | **WHO**[a,c] | **EU**[a,b] |
|---|---|---|---|
| PM$_{10}$ | 1 day | 45 µg m$^{-3}$ * | 50 µg m$^{-3}$ ** |
| | Calendar year | 15 µg m$^{-3}$ | 40 µg m$^{-3}$ |
| PM$_{2.5}$ | 1 day | 15 µg m$^{-3}$ * | - |
| | Calendar year | 5 µg m$^{-3}$ | 25 µg m$^{-3}$ |
| Pb | Calendar year | 0.5 µg m$^{-3}$ | 0.5 µg m$^{-3}$ |
| As | Calendar year | RL: 6.6 ng m$^{-3}$ | 6 ng m$^{-3}$ |
| Cd | Calendar year | 5 ng m$^{-3}$ | 5 ng m$^{-3}$ |
| Ni | Calendar year | RL: 25 ng m$^{-3}$ | 20 ng m$^{-3}$ |

*maximal 3-days exceedance per year (99th percentile of an annual distribution)
**maximal 35-days exceedance per year (approx. 90th percentile of annual distribution)
RL = reference level
Source: [a]EEA report 2020 [19], [b]EN14902:2005 [86], [c]WHO (2021) [87]

The analytes currently monitored in air quality networks are a good proxy for air pollution. However, a lot of other problematic pollutants exist, which also contribute to the toxicity of PM and are not included (*e.g.* phenols, other toxic elements, nitro-PAHs). Furthermore, source apportionment models perform better with multi-element input data, requiring more detailed elemental composition information to accurately identify specific sources. Determination of more PM components would eventually improve prediction and source apportionment models, and provide better information, so that more targeted actions can be planned and applied for mitigating specific emissions and substantially improving air quality. However, identification of more analytes in a complex PM matrix for monitoring or research purposes requires accurate and precise determination methods. The standard methods provided by regulatory agencies are limited only to the components currently involved in routine monitoring processes. Therefore, the development of alternative methods covering new or more analytes at a time is beneficial.

## 1.3 Techniques for PM Determination

In research, many different techniques are used and new methods are constantly being developed. The chemical composition of PM can be measured on-line, where information is gathered on-site in real-time, or off-line, where samples need to be first collected and later analyzed in a different facility. On-line and semi-online (*i.e.* samples are collected for a short period of time – minutes to hour, and analyzed on site) measurements provide information about diurnal variations and allow for the identification of site-specific patterns (*e.g.* traffic rush hours), however, on-line measurements are often limited by instrumentation capabilities (continuous, automated operation without operator presence) and sensitivity. On-line or semi-online determination is currently available for total carbon (TC), BC and BrC with Aethalometer [88] coupled with a Total Carbon Analyzer [89] (*i.e.* Carbonaceous Aerosol Speciation System (CASS, Magee Scientific)), ions with particle into-liquid sampler (PILS) coupled with ion chromatography (IC), or monitoring instrument for aerosol and gasses (MARGA), metals with Xact Ambient Metals Monitor (based on XRF technique; Salibri Cooper Inc), organic PM composition with a filter inlet for gases and aerosols (FIGAERO) coupled with a mass spectrometer [90], aerosol mass spectrometer (AMS), or aerosol chemical speciation monitor (ACSM) [57, 91]. However, on-line instruments for organic composition determination still cannot provide targeted molecular characterization.

Traditionally, off-line techniques are used for PM analysis. Although sampling times can be short, theoretically providing comparable information to semi-online techniques, at least 12 h sampling is usually needed to gather enough material to exceed limits of detection (LODs). Therefore, daily (24 h) samples are most commonly collected, averaging whole-day aerosol concentration and allowing for inter-day/seasonal comparisons. This approach is also used in monitoring agencies, since more analytes can or need to be determined in a single PM sample.

The off-line analytical techniques used to determine of elemental and phenolic composition are discussed below.

### 1.3.1 Sample collection and PM mass concentration determination

Due to a very dilute aerosol system, in which a constant equilibrium exists between all three physical phases (gas, solid and liquid), sampling of atmospheric PM is not as straightforward as one would imagine. Traditionally, PM sampling is performed by a PM sampler, which draws the air through a filter on which particles are collected. Large air volumes are usually required so that PM particles are concentrated enough on a sampling media. Therefore, when talking about PM samples, this usually does not refer to PM alone, but typically denotes PM collected on a matrix (Figure 3).

In research, distribution of analytes by different size fractions is interesting to study, especially if fractions can be collected simultaneously, so that the samples are representative of the same aerosol. Here, two instrument choices exist: (i) dichotomous PM sampler with a $PM_{10}$ inlet and a virtual impactor to separate coarse ($PM_{2.5\text{-}10}$) and fine particles ($PM_{<2.5}$) on separate filters [92], and (ii) cascade impactor, which can divide more than two different fractions of PM, so that every PM fraction is deposited on a separate sampling medium [83, 93].

The collected fraction of suspended PM (*e.g.* $PM_{10}$, $PM_{2.5}$) is determined by a sampling head (impactor-based inlet), which cuts off sizes bigger than the size determined by its inlet. This sampling procedure is also used for monitoring purposes and thus specified in detail in standard EN12341:2014, where special attention is given to possible artefacts that could originate from inappropriate sampling, storage, transport, or sample handling and should be considered with caution. Positive artefacts can occur due to absorption of volatile compounds (*e.g.* ammonia, nitrogen dioxide, organic gases) or adsorption of semi-volatile compounds and water from the gas, while negative artefacts are typically due to volatilization of semi-volatile compounds and water off the filter. With assuring optimal temperatures (during sampling, storage, transport), relative humidity, and flow rate, losses of semi-volatile compounds are limited. Moreover, if the instructions in EN12341 are followed, the losses due to volatilization can be considered zero by convention. Other losses of particles can happen in the pipe work or by transmission through the filter, but are considered negligible in a standard procedure.

It is also important that filter material used for the collection of PM meets certain requirements: (i) retention efficiency for particles with the aerodynamic size of 0.3 μm is at least 99.5 %, (ii) sufficient integrity is retained during sample handling, (iii) pressure drop during the collection should not hinder the flow rate, (iii) sufficient collection capacity is assured to avoid clogging, (iv) water sorption is limited, (v) static charge can be removed before weighting, and (vi) appropriate characteristics for further analysis (low impurities in chemical analysis, high thermal stability in OC/EC analysis, well retained integrity for gravimetry analysis *etc.*). Commonly used filter matrices are quartz fiber, glass fiber, polytetrafluoroethylene (PTFE), PTFE coated glass fiber, cellulose fiber, polycarbonate, and others, depending on what characteristics are needed for further analysis. For the OC/EC analysis by thermal optical analysis (TOA), filter matrix has to withstand very high temperatures, which makes quartz-fiber filter the only viable choice and is therefore the most commonly used filter in monitoring agencies.

Figure 3: PM collected on quartz fiber filters in different seasons.

Typically, total PM mass is determined gravimetrically by weighting the filter before and after the collection of PM. To avoid biases due to absorption or desorption of water vapor, which could importantly influence the mass of the sample (note: collected PM mass is very small compared to the filter mass), conditioning at controlled temperature and humidity for sufficient amount of time is prescribed to reach equilibrium at the same conditions before and after the sampling.

### 1.3.2 Elemental determination

Elemental composition of PM is most commonly determined off-line, after the sampling on a filter. The analytical methods for elemental determination can be divided into two groups in respect to the required physical state of the sample for the analysis:

- conventional analysis of samples in a liquid form (*i.e.* PM extracts), after a pre-treatment of PM samples with microwave digestion: *e.g.* inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma optical emission spectrometry (ICPOES), graphite furnace atomic absorption spectroscopy (GFAAS), flame atomic absorption spectroscopy (FAAS), ion-selective electrodes, and stripping voltammetry, and
- direct analysis of solid PM samples without any pretreatment: *e.g.* laser ablation ICPMS (LA-ICPMS), X-ray fluorescence (XRF) and its variations, particle-induced X-ray emission (PIXE), instrumental nuclear activation analysis (INAA), and laser-induced breakdown spectroscopy (LIBS).

All these methods have their benefits and drawbacks and their detailed description and comparison is found in our review article (Chapter 3.1). In short, EU prescribes a standard method for environmental agencies with microwave digestion to fulfill the required traceability stated by European Directives and to assure inter-laboratory comparability across different countries. However, this method has many weaknesses and is expected to be updated in the recent future to catch up with the advancement in atmospheric chemistry research. Many alternative methods capable of direct analysis of solid samples have already been successfully applied in research, however, certain shortcomings still prevent them from becoming a substitute of the standard method. LA-ICPMS, which was the method of our choice, is not yet a widespread technique, but has a great potential to be used for routine air-quality monitoring someday.

#### 1.3.2.1 Standard method (EN14902:2005)

As already mentioned, EU legislation dictates the measurement of four elements (*i.e.* As, Cd, Ni, and Pb) in ambient air (Directive 2004/107/EC, and 2008/50/EC) and prescribes the standard method for their determination (EN14902:2005) to be used for air-quality monitoring purposes. The method determines the sampling procedure of $PM_{10}$ fraction of ambient PM (according to EN12341:2014) with a preferable filter material (*i.e.* quartz fiber, cellulose nitrate, or cellulose acetate filters), sample pre-treatment by microwave digestion (MW) using concentrated nitric acid ($HNO_3$) and hydrogen peroxide ($H_2O_2$), and analysis with ICPMS or GFAAS, as well as a guidance for providing traceability and meeting strict analytical requirements (*i.e.* procedure for assessing quality assurance/quality control, estimated uncertainty, performance characteristics) [86].

Besides the mentioned four elements, the more recent Directive (EU) 2016/2284 directs to report concentrations of some other elements in atmospheric PM as well (*i.e.* Cr, Cu, Se, and Zn), for which the standard method is not provided. Normally, EN14902 is used for the determination of all elements (more than specified), even though this standard method does not guarantee the accuracy and sufficient digestion efficiency for other elements. This brings us to the weaknesses and drawbacks of the current standard method, which are mostly due to the MW pre-step (details in 3.1):

- the prescribed digestion protocol does not provide complete digestion of quartz fiber filters and also puts under question digestion efficiency of some specific PM matrices (*e.g.* Saharan dust), preventing total multielement determination,
- the additional sample pre-treatment step introduces a risk of sample contamination or loss of volatile elements,
- sample loss can occur at events of vessels explosion, due to uncontrolled increase of pressure inside the vessels caused by unexpected PM compositions or concentrations,
- MW digestion is a time-consuming step,
- the elements of interest are usually present at trace concentration levels, meaning that high-purity reagents have to be used to provide sufficiently low LODs; however, the digests still need to be diluted prior to analysis to be compatible with the ICPMS instrumentation, which consequently elevates LODs even further,
- the necessary concentrated reagents eventually end up as toxic waste, which is not a neglectable amount considering regular monitoring all around the globe, and the number of air-quality monitoring sites is still expected to grow in less developed countries.

Although the described standard method is appropriate for the purpose it was developed, with the advancement of knowledge and development of new analytical instrumentation and analytical methods, multielement determination can be achieved with direct determination from a solid sample nowadays, without burdening the environment. The movement in this direction has already been made in EU Scientific and Technical Research Report [94], where energy-dispersive XRF (EDXRF) has been discussed as an alternative method for the determination of elements in PM, particularly for use in source apportionment studies, for which the information of multi-element composition is paramount.

### 1.3.2.2 LA-ICPMS

LA coupled with ICPMS is a relatively modern technique used in analytical chemistry, where sample introduction into ICPMS is performed by an LA system. It is an alternative to classical ICPMS liquid introduction systems, where elemental concentrations in solid samples are measured without the need for microwave digestion.

The main parts of an LA system are a laser beam generator, an ablation chamber and a transport path of the ablated particles to the ICPMS (Figure 4). A sample is placed in a gas-tight ablation chamber, which is filled with helium as a carrier gas. A focused laser beam ablates the material with pulsed shots hitting the surface of the sample, generating vapor, particles and agglomerates, *i.e.* aerosol of the ablated material above the sample. The generated aerosol is continuously flushed with the carrier gas to the ICPMS, where it is atomized and ionized in a plasma, separated by mass and charge, and detected with a mass selective detector [95].

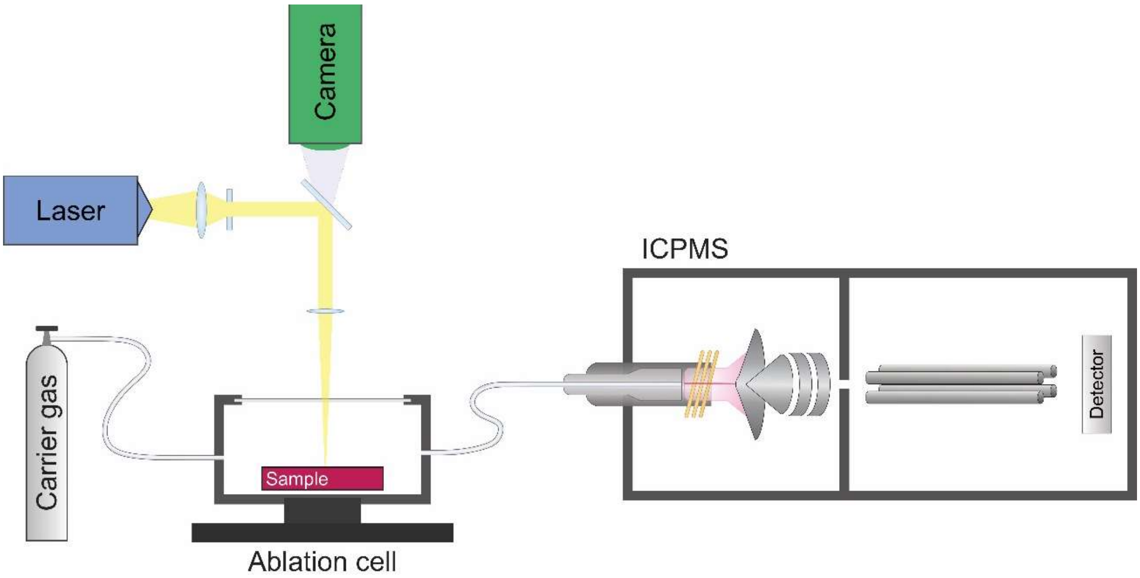


Figure 4: Schematic representation of the LA-ICPMS system.

Different types of lasers exist, which mainly differ by wavelength (*e.g.* 1064, 266, 213, 193 nm, etc.), laser production mechanism (*e.g.* excimer or solid state), irradiation time (*i.e.* nanosecond or femtosecond pulse width), and price. In the past, long wavelength (visible and infrared) laser beams were used, including in the first attempts of ablating PM [96-99]. With the development of LA technique, it has been demonstrated that shorter wavelength lasers better suit the purpose in general (*e.g.* cause less elemental fractionation), so nowadays even in the analysis of PM samples, the most commonly used lasers are 193 nm argon fluoride excimer (ArF*) and 213 nm Nd:YAG solid state lasers [93, 100-102].

Ablation is influenced by the LA system, as well as sample characteristics. Unfortunately, no research has been made by directly comparing LA systems for the ablation of PM samples, however, when comparing NIST 610-614 glass samples, the size distribution of ablated particles is different, depending on the laser type. The 193 nm laser produced particles mostly in the small size range (below 0.4 µm), whereas lasers with higher wavelengths (213 and 266 nm) produced wider size distributions including larger particles, even around 1 µm. Large particles, however, could be problematic, since they may get deposited next to the crater base and are not transported to ICP. Also, if they arrive to plasma, their atomization and ionization may not be efficient [103]. Particle size distribution is also affected by sample characteristics (*e.g.* transparency). In more transparent reference materials (RM) NIST 612 and 614, 193 nm lasers produced distinctively narrower size distribution than 213 and 266 nm lasers, whereas in more opaque RM NIST 610, particle size distributions were comparable for 193 and 213 nm lasers, and performed better than 266 nm laser [104]. Similar, Brown, et al. [105] ablated PM samples using 266 nm LA system and had some problems with large particles generated, which worsened the repeatability of the measurement. As a solution, an in-line filter to remove the large particles was installed, which significantly improved repeatability of the measurement [106, 107]. This problem, however, was not reported by other authors using 193 or 213 nm LA systems [100, 102], but to be able to attribute this effect to the ablation with different wavelengths, direct comparisons based on the same PM samples would have to be made.

Similar to the particle size distribution, laser stability is also affected by the laser wavelength. When comparing NIST glass standards, 193 nm laser performed best and 266 nm laser was drifting in time in all NIST glass RM. The stability of 213 nm laser was dependent on sample transparency, performing best in opaque NIST 610 and worse in more transparent NIST 614 [103]. The stability of the laser is important when planning to measure a large set of samples, like in air pollutants monitoring. Therefore, when choosing the best laser type for these purposes, this aspect should be carefully considered.

From the literature survey we can conclude that most researchers used flat filter matrices, like PTFE [93, 97, 98, 108-110], polycarbonate [111], cellulose nitrate membrane [99, 112], and cellulose ester [105-107, 113] filters, since it is easier to focus the LA beam on a flat surface, which is needed to provide optimal ablation. Quartz fiber filters, which are most universal for atmospheric analyses and most often used in air-quality monitoring, because they allow for many complementary analyses to be performed on the same sample, are unpopular for LA due to their uneven surface. Only two papers have investigated PM on quartz fiber filters; in the first case from 1994, nowadays obsolete 1064 nm LA system was used [96], and in the second case, PM samples were collected by an impactor and only the smallest size stage was analyzed [102]. Furthermore, in most other relevant studies, impactor was used for sample collection [93, 101, 102, 109-111, 114], whereas particles were often collected in piles and not over the whole filter area, or obsolete 1064 and 266 nm LA systems were used [96-99, 105-107]. However, none of the papers describes a complete method development, especially for quartz fiber filters, leaving the questions of quantification and homogeneity for further investigation.

Quantification of results is one of the biggest challenges in LA-ICPMS, as matrix-matched RM is needed to nullify different fractionation effects between a sample and the RM used for quantification. Theoretically, in the case of PM samples, every type of filter matrix needs its own standardized RM. Furthermore, different ways of PM collection (*e.g.* classical PM sampler vs. impactor) or significantly different PM compositions also do not necessarily behave as matrix-matched materials.

The main problem in the calibration is that certified matrix-matched RM is not always commercially available, which is also true for PM on quartz fiber filters with certified elemental composition. Some alternative procedures have been tested, where NIST standardized reference material (SRM) 1648 (urban PM in dust form) was compressed to pellets, adhered to the surface, or deposited on a filter, but the reproducibility of these calibration methods was not adequate or they faced a problem with filter saturation and insufficient linearity [97, 107]. Another alternative was by spiking the filters with liquid standards (*e.g.* dried droplet approach on blank filters or samples, or spiking of the whole blank filter area). The elements, however, were shown non-homogeneously distributed throughout the filter, exhibiting chromatographic effect and different sensitivity [99, 107, 109, 113, 115], which would cause inaccurate quantification if only one part of the standard was ablated. This error, however, could be avoided with the ablation of the whole dry droplet/standard [115], but this would be too time-consuming in the case of quartz fiber filters. Until now, there has been no appropriate calibration procedure for the routine analysis of ambient aerosol samples with LA-ICPMS. Therefore, the lack of repeatability and accuracy in current approaches was calling for further research.

The second challenge which needs to be addressed is the homogeneity of the samples. For PM samples, the homogeneity of PM distribution on the filter surface is generally accepted. However, LA generates very small laser beams (only a few μm in size) and at this level the homogeneity may not always be taken for granted, since PM is a mix of individual particles of different sizes and compositions.

Tang, et al. [102] found higher element concentrations at the edge of a PM sample compared to the center of the filter and attributed the observed chromatographic effect to ablation, since the filter edge is looser and easier to ablate than the interior. However, non-homogeneous deposition of PM was also observed on impactor foils, the measured concentrations being higher in the center and dropped quickly along the radius of the filter, stabilizing about 10 mm from the center [105]. On the other hand, some authors described relatively uniform PM deposits on filters, with 10 % variation between the measurements in different locations [99].

In addition, LA has the ability to analyze spatial distribution of elements, whereas the analysis can include only a few spots [97, 108] or a full scan of the surface providing 2D or even 3D images when measuring additional layers [116]. Therefore, due to all the different possibilities, a sampling protocol needs to be defined during the development of a LA-ICPMS method for the determination of elemental composition of PM samples, which would take into account (in)homogeneity of the samples and provide accurate results.

Although a few attempts have already been made to analyze PM samples by LA-ICPMS, no successful method has been reported to date for PM on the most widely used quartz fiber filters including detailed method development and parameter optimization, homogeneity assessment, and quantification procedure. Such a developed method would be of great benefit and would have the potential to serve as a green alternative in air-quality monitoring.

### 1.3.3 Organic aerosol characterization

Organic components are often the major and ultimately the most undefined constituent of atmospheric PM, therefore, many different approaches for their characterization are possible depending on the desired information. The concentration of OC is determined by TOA, which differentiates OC from EC based on their different thermal properties and light reflectance/transmittance characteristics [117, 118]. Optical properties of atmospheric aerosols (*e.g.* wavelength specific transmittance and absorption) can be further exploited for speciation of carbonaceous aerosols by combining measurements of spectrally resolved optical absorption with measurements of total carbon concentration (TC) in high time resolution (*i.e.* CASS system), to differentiate between BC, BrC and non-absorbing POA and SOA, and to apportion BC sources to fossil fuel and biomass burning [88, 119, 120]. Moreover, for online molecular speciation of organic aerosols, different techniques are applied, such as AMS, ACSM, FIGAERO with chemical ionization mass spectrometer (CIMS) *etc.*, which provide information on the molecular composition and/or contained chemical groups in real time (*e.g.* carbohydrate ions with a different number of atoms, sulphate and nitrate functional groups), typically dividing contained components into groups of hydrocarbon-like and oxygenated organic aerosol, cooking organic emissions, and biomass burning.

However, for the identification of emission markers, studies of atmospheric reactions and processes, and chemical toxicity assessment, targeted molecular-level characterization is needed. PM is a mix of various analytes and targeted analysis requires supreme chromatographic separation (*i.e.* gas chromatography (GC) or liquid chromatography (LC)) followed by a specific mass spectrometric (MS) detection. Chromatographic techniques are applied off-line, after the collection of PM on a filter, liquid extraction, and most often also follow a concentration step. Extraction reagents are chosen based on analyte solubility and compatibility with analytical instruments (if they are not later replaced in the concentration step) and PM extraction procedure is sometimes accompanied by elevated temperature and/or pressure, microwave or ultrasound treatment. Concentrations of organic compounds in PM are typically very low, therefore, a pre-concentration step, such as solvent evaporation or solid-phase extraction are often applied. Sample pre-treatment steps are often constrained with the properties of target analytes (*e.g.* volatility, solubility, thermal stability) and can result in analyte loss (*e.g.* analyte degradation, co-evaporation with solvent), which has to be carefully examined.

GC techniques are preferentially used for the determination of volatile species (*e.g.* PAHs, alkanes, ketones, aldehydes, monoterpenes). Low-volatility analytes, however, cannot be simply determined by GC-MS and require additional derivatization step (*e.g.* sylation) to increase their volatility [121-123]. Besides traditional liquid extraction and GC-MS determination, direct analysis of solid PM samples with use of a thermal desorption (TD) unit is also possible, which has been shown especially useful in the case of PAH and nitroPAH, as they are nonpolar compounds with high boiling temperature and, therefore, ideal for this technique [124]. TD-GC-MS requires less sample as it circumvents all the pre-treatment steps, however, polar and thermally labile compounds still need to be analyzed with other techniques. Therefore, for polar PM components with limited volatility, LC-MS is a technique of choice with more operational capabilities.

#### 1.3.3.1 LC-MS

Because of its specificity, accuracy, precision, and sensitivity, LC-MS is often used in atmospheric chemistry research. The (ultra) high performance liquid chromatography ((U)HPLC) enables sufficient separation of a complex PM matrix for the following mass spectrometric detection, where the commonly used high resolution MS or tandem mass spectrometer (MS/MS) provide specific mass determination with a limited number of interferences.

Many organic PM components have already been determined by LC-MS, such as nitrated phenols and other phenolic derivatives [76, 83, 125-129], amines [130], carboxylic acids [131], humic-like substances [132], monosaccharides [133], trenbolone acetates [134], pesticides [135], drugs of abuse [136], PAH [137] and oxygenated PAHs [138]; however, to the best of our knowledge only one paper reports on the determination of simple phenols in ambient PM [82]. Based on our experiences, simple phenols are difficult to be simply determined with LC-MS due to very poor ionization efficiencies, especially at the concentrations found in atmospheric PM. Furthermore, the simple phenols are semi-volatile, therefore, any pre-concentration steps should be well thought through as they could result in substantial analyte loss.

In general, to enhance ionization efficiency, analytes can be derivatized with a group with good ionization efficiency. For various analytes with the phenolic functional group, derivatization agents such as dansyl chloride (DnsCl), pentafluorobenzylbromide (PFBBr), 1,2-dimethylimidazole-4-sulfonyl chloride (DMISC), pyridine-3-sulfonyl chloride (PS), benzoyl chloride, dabsyl chloride (DABS-Cl), 4-(dimethylamino)-benzoic acid (DMBA) have been used [139]. In research papers, DnsCl enabled detection of some of our targeted simple phenols, when targeting other compounds in different complex matrices. Phenol has been detected during the bulk analysis of metabolites in cerebrospinal fluid [140], whereas phenol and cresols have been detected during the analysis of metabolites in urine samples [141] and in the analysis of phenolic compounds in river and sediment samples [142]. DnsCl has also been used for enhancing the detection of other phenolic metabolites in urine [143], estrogens in cerebrospinal fluid [144], bisphenols in river water and sediment samples [145], and bisphenol A in human saliva [146].

Next to a few times enhanced ionization efficiency (reported from 10 to a 1000-fold) [141, 142], DnsCl has also other benefits in phenols determination by HPLC, as is extended retention on a column resulting in easier separation of relatively polar compounds with reverse-phase chromatography, improved stability and reduced in-source fragmentation, which provides more stable and intense fragment ions and eases quantification [147]. Derivatization with DnsCl could thus provide a solution in the determination of simple phenols with LC-MS, possibly circumventing the problematic pre-concentration step; however, a new method needs to be developed, *i.e.* derivatization reaction needs to be optimized for the target phenols in a PM matrix and parameters for LC-MS have to be adapted accordingly.

# Chapter 2

# Research Aims and Hypothesis

The goal of the doctoral dissertation is to develop two new analytical methods for better characterization of PM collected on most universally used quartz fiber filters. The first method by LA-ICPMS will be used for elemental determination of PM and will allow for multi-element determination circumventing many drawbacks of the current widely used standard MW/ICPMS method. The developed LA-ICPMS method will be compared with MW/ICPMS to assess its performance in terms of accurate determination of PM samples and suitability for the monitoring purposes. In this sense, the LA-ICPMS method will be further adapted for a more affordable 213 nm LA system, and the performance of excimer193 nm and solid state 213 nm LA systems will be compared and evaluated. At the end, the developed LA-ICPMS method will be applied to a large number of PM samples collected in different seasons, which will be done in the frame of a larger project assessing the influence of PM pollution on cultural heritage.

The second method will be developed for the determination of simple phenols in PM, which has rarely been studied. The method will be particularly helpful for studying phenolic transformations in the atmosphere, the mechanisms of which are still not well understood. Pre-treatment steps (*i.e.* extraction and derivatization) will be carefully selected, avoiding evaporation of the semi-volatile compounds of interest. The method will be optimized using liquid standards and later applied to real ambient PM samples from different seasons to assess phenolic content in different seasons and connect it to distinct pollution sources.

**Hypotheses:**

1. Determination of PM elemental composition directly from quartz fiber filters is feasible with LA-ICPMS and allows for accurate determination of more than 4 elements simultaneously.
2. The performance of the LA-ICPMS method is comparable to or better than the standardized MW/ICPMS method and has the potential to replace the current burdensome MW/ICPMS method in air monitoring agencies.
3. Laser ablation analysis of PM is feasible also with a more affordable solid state 213 nm laser, which reduces the initial investment during the transition to a greener LA-ICPMS method.
4. In Ljubljana, the concentration of elements of anthropogenic origin is higher in winter due to heating purposes or climate features (*e.g.* temperature inversions).
5. Simple phenols in PM can be extracted and analyzed by LC-MS without a sample pre-concentration step.

6. Concentrations of simple phenols in PM are higher during biomass-burning seasons (winter, partly autumn/spring) compared to warmer months since biomass burning is the main source of phenols in the air.

# Chapter 3

# Scientific Publications

The dissertation consists of one review article, three original scientific articles and one manuscript. Article 1 (Section 3.1) presents the state of the art in the determination of elements in PM and critically assesses the standard method according to the EU directive (*i.e.* MW/ICPMS), which is currently in use for routine air quality monitoring in Europe. The main focus is on alternative methods capable of the direct analysis of solid PM samples without the need for MW pre-treatment step, and on the evaluation of their potential to replace the standard method in the future. This paper also presents a good introduction, explaining in detail why the current standard method is so problematic and why new, better methods and further research are needed. Then, in Article 2 (Section 3.2), a new method for the elemental determination of PM with LA-ICPMS is presented, which covers the first hypothesis by evaluating the feasibility of accurate elemental characterization of PM samples collected on quartz fiber filters by LA-ICPMS with multi-element capabilities. Furthermore, the article also compares the developed LA-ICPMS method with the standardized MW/ICPMS method, targeting Hypothesis 2. The second LA instrument is applied and compared in Manuscript 3 (Section 3.3), in which the method for the elemental determination of PM adapted for a more affordable solid state 213 nm LA system is presented and the performance of 213 nm and 193 nm LA systems is compared, in line with Hypothesis 3. Article 4 (Section 3.4) represents application of the developed LA-ICPMS method on a large number of PM samples collected in different seasons (Hypothesis 4), and connects airborne PM pollution with the potential emission sources responsible for the damage caused to calcareous cultural heritage objects due to PM deposition on their surface. The second part of the dissertation presenting the new method developed for the determination of simple phenolic compounds in PM by LC-MS/MS is covered by Article 5 (Section 3.5), in which the method is also tested on ambient PM samples collected in different seasons, in line with Hypotheses 5 and 6.

Furthermore, during the PhD studies, I collaborated in two projects, which resulted in additional two papers relevant for the dissertation. With the colleagues from Zagreb we published a paper about air pollution levels at the Mediterranean coast (Appendix A.1), in which I contributed with the analysis of nitrophenols in ambient PM samples, and bulk and wet PM deposits. Moreover, with colleagues from Ljubljana we investigated the influence of Bakelite microplastics on aquatic microorganisms (Appendix A.2), where the developed method for the determination of simple phenols in PM extracts was applied to other environmental samples to determine phenols in leachates.

Therefore, the present dissertation provides two new methods for the characterization of PM, first for the direct elemental determination of PM collected on quartz fiber filters by LA-ICPMS and second for the determination of simple phenols in PM by LC-MS/MS. The development of these methods is presented in detail, together with their application to real-life ambient PM samples demonstrating practical use in research.

## 3.1 Article 1: Critical Review on the Development of Analytical Techniques for the Elemental Analysis of Airborne Particulate Matter

*Published: Ogrizek M., Kroflič A., Šala M., (2022). Trends in Environmental Analytical Chemistry, 33, e00155.*

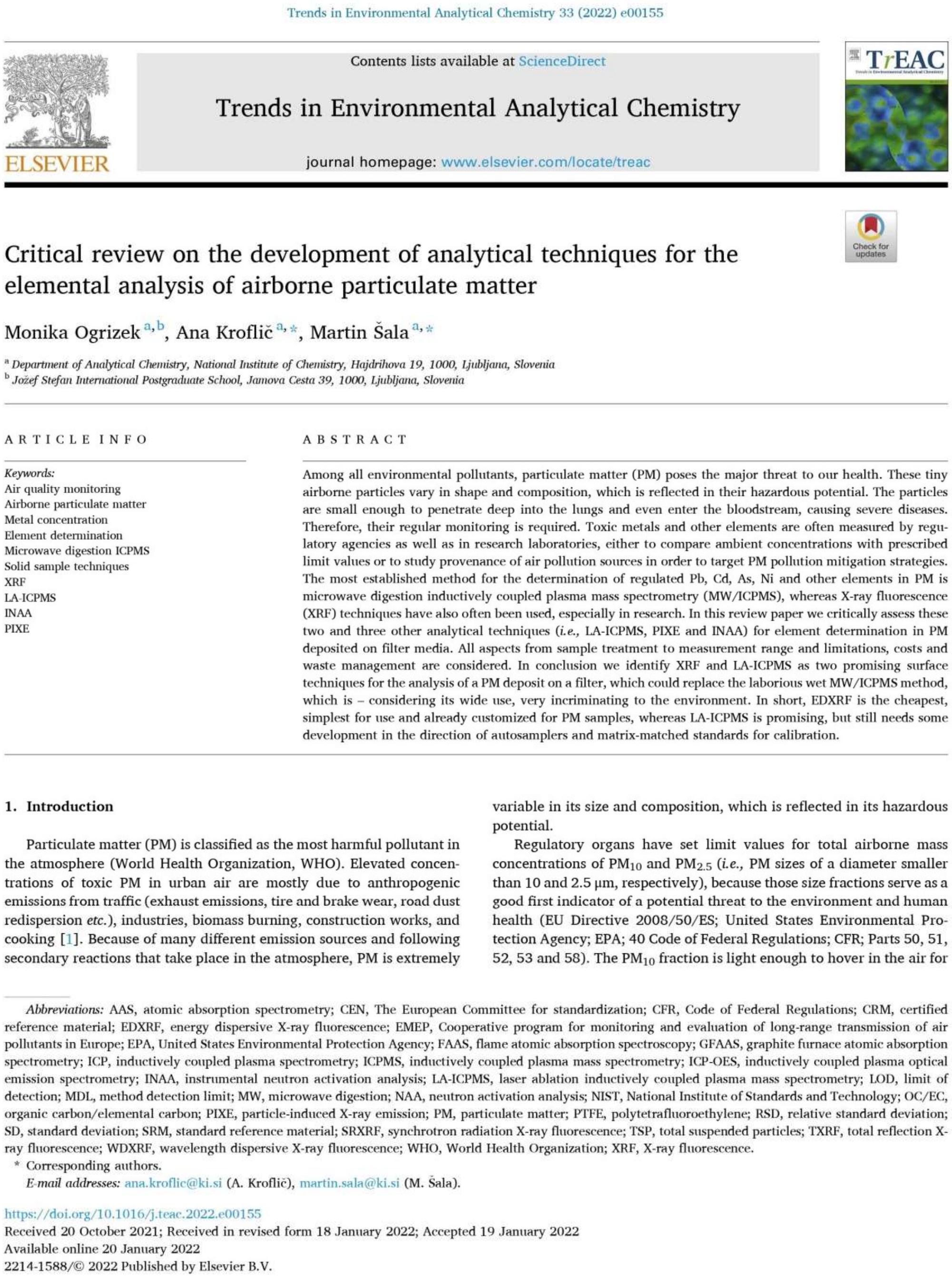
PM is one of the most dangerous air pollutants. Its toxic properties are dependent on the particle size and composition. Four trace elements (*i.e.* As, Cd, Ni, Pb) are regularly monitored by European environment agencies with a standard method (*i.e.* microwave digestion and ICPMS; EU directives 2004/107/EC and 2008/50/EC), which assures accurate determination of the four elements but also has a lot of drawbacks. Therefore, we have recognized the need to update the prescribed method, so that it would allow for accurate determination of more elements, would be less laborious and would not burden the environment with toxic waste.

Air quality is of paramount importance for the humanity, so many alternative techniques for element determination in PM are being tested and developed in the scientific community. The selection of an analytical technique always depends on the sample type, research question and the accessibility of the equipment. Specialized instrumentation for on-line determination of elements in PM has been developed (*i.e.* Xact ambient metals monitor), which provides information on the elemental levels in the air in real time and allows for studying diurnal variation of air pollution. However, most dangerous elements are usually present in the air at very low concentrations. This hinders their on-line determination, since enough PM material needs to be collected to assure concentrations above the LOD. Therefore, traditional off-line analysis of PM samples typically collected for 24 h on a filter is still the preferred way for air quality monitoring purposes.

When considering the standard method, the major drawbacks originate from the microwave digestion step, which is required for the pre-treatment of a PM sample providing liquid sample needed for the injection into ICPMS. Therefore, techniques and methods capable of the direct analysis of PM on a filter have the highest potential to replace the current standard method in the future. INAA, PIXE, LA-ICPMS, and XRF including its variants (*i.e.* EDXRF, wavelength dispersive XRF (WDXRF), synchrotron radiation XRF (SRXRF), and total reflection XRF (TXRF)) have been recognized as possible candidates and their application on PM samples has already been tested. Except for EDXRF, which has already been approved as a standard method by U.S. EPA for the determination of lead (Pb) in $PM_{10}$ and its use is recommended for source apportion purposes in EU, these analytical approaches have only been used in research so far.

In this paper we review the relevant literature and critically assess the listed techniques capable of direct determination of PM on filters and compare them to the current standard method in EU. Sample type and preparation procedure, number of elements determined and their concentration range, filter matrix, sample throughput (*e.g.* time required for the analysis), calibration practices, LOD, accuracy and precision, availability and cost, and waste management are specifically considered. In the review, we conclude that EDXRF and LA-ICPMS are both green methods and have the highest potential for replacing the MW/ICPMS method in the future. EDXRF has its advantages in calibration, already available automatization, and affordability, while LA-ICPMS has benefits in lower LODs and capabilities in the determination of PM on quartz fiber filters. EDXRF is limited with the type of filter matrices, which often results in the need for separate sampling for the elemental analysis. LA-ICPMS, on the other hand, still falls behind with the development of autosamplers and established calibration protocols especially for quartz fiber filters (*i.e.* matrix-matched standard material certified for the elemental composition is not yet available). PIXE has the advantage of being non-destructive, however it is a nuclear technique and requires special infrastructure and strict safety measures, limiting its wide availability. INAA was also not recognized as promising for the purpose of regular air-quality monitoring. Although it is capable of analyzing various filter matrices, including quartz fiber filters, it is very sensitive to filter impurities and, additionally, it is time-consuming, requires special infrastructure (*i.e.* nuclear reactor) and safety measures, and produces radioactive waste. However, since it is an absolute method, we suggest exploiting it for the characterization of standard materials, which are paramount in other techniques.

The motivation behind this article was to examine the possibilities of placing LA-ICPMS along with other analytical techniques for the elemental determination of PM, to find its flaws and benefits in comparison with other techniques and promote it for this particular application.



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# Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter

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ABSTRACT

Among all environmental pollutants, particulate matter (PM) poses the major threat to our health. These tiny airborne particles vary in shape and composition, which is reflected in their hazardous potential. The particles are small enough to penetrate deep into the lungs and even enter the bloodstream, causing severe diseases. Therefore, their regular monitoring is required. Toxic metals and other elements are often measured by regulatory agencies as well as in research laboratories, either to compare ambient concentrations with prescribed limit values or to study provenance of air pollution sources in order to target PM pollution mitigation strategies. The most established method for the determination of regulated Pb, Cd, As, Ni and other elements in PM is microwave digestion inductively coupled plasma mass spectrometry (MW/ICPMS), whereas X-ray fluorescence (XRF) techniques have also often been used, especially in research. In this review paper we critically assess these two and three other analytical techniques (*i.e.,* LA-ICPMS, PIXE and INAA) for element determination in PM deposited on filter media. All aspects from sample treatment to measurement range and limitations, costs and waste management are considered. In conclusion we identify XRF and LA-ICPMS as two promising surface techniques for the analysis of a PM deposit on a filter, which could replace the laborious wet MW/ICPMS method, which is – considering its wide use, very incriminating to the environment. In short, EDXRF is the cheapest, simplest for use and already customized for PM samples, whereas LA-ICPMS is promising, but still needs some development in the direction of autosamplers and matrix-matched standards for calibration.

## 1. Introduction

Particulate matter (PM) is classified as the most harmful pollutant in the atmosphere (World Health Organization, WHO). Elevated concentrations of toxic PM in urban air are mostly due to anthropogenic emissions from traffic (exhaust emissions, tire and brake wear, road dust redispersion *etc.*), industries, biomass burning, construction works, and cooking [1]. Because of many different emission sources and following secondary reactions that take place in the atmosphere, PM is extremely variable in its size and composition, which is reflected in its hazardous potential.

Regulatory organs have set limit values for total airborne mass concentrations of $PM_{10}$ and $PM_{2.5}$ (*i.e.,* PM sizes of a diameter smaller than 10 and 2.5 μm, respectively), because those size fractions serve as a good first indicator of a potential threat to the environment and human health (EU Directive 2008/50/ES; United States Environmental Protection Agency; EPA; 40 Code of Federal Regulations; CFR; Parts 50, 51, 52, 53 and 58). The $PM_{10}$ fraction is light enough to hover in the air for

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*Abbreviations:* AAS, atomic absorption spectrometry; CEN, The European Committee for standardization; CFR, Code of Federal Regulations; CRM, certified reference material; EDXRF, energy dispersive X-ray fluorescence; EMEP, Cooperative program for monitoring and evaluation of long-range transmission of air pollutants in Europe; EPA, United States Environmental Protection Agency; FAAS, flame atomic absorption spectroscopy; GFAAS, graphite furnace atomic absorption spectrometry; ICP, inductively coupled plasma spectrometry; ICPMS, inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; INAA, instrumental neutron activation analysis; LA-ICPMS, laser ablation inductively coupled plasma mass spectrometry; LOD, limit of detection; MDL, method detection limit; MW, microwave digestion; NAA, neutron activation analysis; NIST, National Institute of Standards and Technology; OC/EC, organic carbon/elemental carbon; PIXE, particle-induced X-ray emission; PM, particulate matter; PTFE, polytetrafluoroethylene; RSD, relative standard deviation; SD, standard deviation; SRM, standard reference material; SRXRF, synchrotron radiation X-ray fluorescence; TSP, total suspended particles; TXRF, total reflection X-ray fluorescence; WDXRF, wavelength dispersive X-ray fluorescence; WHO, World Health Organization; XRF, X-ray fluorescence.

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an extended period of time and it can thus be transported over long distances; while $PM_{2.5}$ is especially important from the health perspective because it is small enough to even enter the bloodstream through the lungs and cause severe diseases [2].

The harmful effect of PM further strongly depends on its composition. PM is a mixture of elemental carbon (often also referred to as black carbon), inorganic salts, organic compounds, trace elements, and water. From the health perspective, the fraction of toxic organic components, which are still largely unidentified, and small amounts of harmful trace metals are of special importance (EU Directive 2004/107/EC and 2008/50/EC). Furthermore, trace elements are also good tracers for air-mass source identification and PM elemental composition is typically considered in a basic dataset for source apportionment studies [3]. Namely, in setting air pollution mitigation strategies, the knowledge of emission sources is necessary to act efficiently and directly on the main sources of the measured pollution.

Due to numerous negative effects of PM in general and therein contained trace elements in particular, air-quality monitoring has been established all around the world and the number of monitoring sites is increasing, including in developing countries. Therefore, it is important to have a sensitive, accurate, fast, multi-element, and a possibly green analytical method for the determination of the elemental composition of airborne PM, to provide as good as possible results with a minimal environmental impact.

Many analytical techniques for the elemental determination exist and suitability of some of them for PM analysis is discussed in this paper (schematic summary in Fig. 1). Trends in analytical techniques for general chemical characterization of PM from 1997 until 2018 are summarized in the review paper by Galvao, et al. [4], and single-PM particle analysis has already been covered by Bzdek, et al. [5]. In our paper, a critical eye is given to the determination of (trace) elements in bulk PM, which is suitable for research as well as regulatory purposes. We describe the advantages and drawbacks of current standardized methods and compare them to other available techniques mostly used for PM analysis in recent years, which, to our knowledge, has not been done before. Moreover, we identify future perspectives and needs in order to utilize sensitive and sustainable analytical techniques especially in routine air quality monitoring for research and regulative purposes.

Among the compared techniques, energy dispersive x-ray fluorescence (EDXRF) was proven the simplest and most accessible, in the form of initial and operation costs, calibration options, and sample throughput, however, quartz fiber filter (most versatile filter matrix) cannot be used for this analysis. Furthermore, the most sensitive of XRF techniques, total reflection x-ray fluorescence (TXRF) requires a thin sample and a smooth surface, thus being often subjected to sample digestion in the sample preparation step, which does not qualify as a substantial improvement compared to the standard method. On the other hand, laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) has the potential for becoming an alternative to the standardized method (as also EDXRF), with some shortcomings (*e.g.* calibration, autosampler) that still need to be overcomed. Particle-induced X-ray emission (PIXE) has very good performance characteristics, however, very high initial cost makes it inaccessible for general environmental laboratories. Instrumental neutron activation analysis (INAA), due to its price and safety restrictions, is also unsuitable for regular use in monitoring agencies, however, due to its specific calibration requirements, it is ideal for developing certified reference materials.

## 2. Standard methods in routine monitoring of PM elemental composition

Limit values for PM and trace elements in ambient air are set to provide sufficient air quality conditions for safe living based on the current situation and state of knowledge. If limitations are being constantly exceeded, additional actions for mitigating air pollution should be established.

WHO has set the guidelines for $PM_{10}$ and $PM_{2.5}$ mass concentrations, while EPA and the authorities of the European Union have set mandatory limits for trace elements in ambient air. The limit values and monitoring programs for the European Union are listed in Directive 2004/107/EC (for As, Cd, Hg, Ni), Directive 2008/50/EC (for PM and Pb), and Directive (EU) 2016/2284 (for Cd, Hg, Pb, As, Cr, Cu, Ni, Se, Zn) where the reduction of national emissions for some other pollutants is also anticipated. On the other hand, based on The Clean Air Act, United States' EPA has only established limit values for PM and one trace element (Pb) so far. The limit values are always expressed in the amount of a trace element in μg per $m^3$ air and set as an annual mean (EU) or a rolling 3 months average (EPA).

In addition to the limit values, regulatory organs also provide standard methods for the determination of trace elements in airborne PM. The purpose of standard methods is to provide robust procedures for obtaining accurate, precise, and reproducible results, to enable traceability, and to eliminate interlaboratory variability. Standard methods serve as a tool for data comparison between different laboratories/countries/regions, which is very important for globally affecting air pollutants that can travel long distances, such as PM is. However, with the advancement of knowledge, instrumentation, and measurement procedures, standard methods are expected to be periodically upgraded, to provide more and better information in accordance with scientific

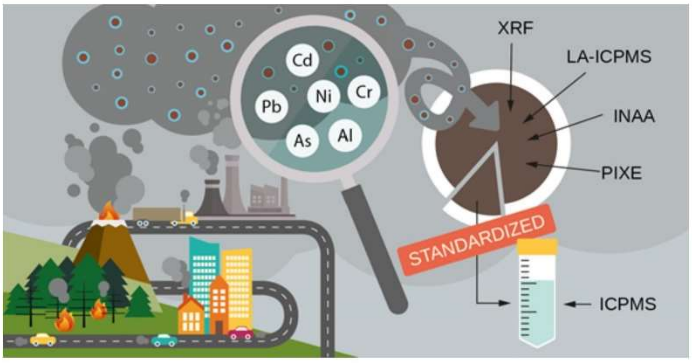

**Fig. 1.** The origin of PM and the most promising methods for the determination of its elemental composition.

achievements.

### 2.1. *CEN (European Committee for Standardization)*

In 2005, CEN published a Standard method for the measurement of Pb, Cd, As, and Ni in the $PM_{10}$ fraction of suspended PM (EN 14902:2005). The standard method prescribes (i) a sampling procedure by an off-line high (HVS) or low (LVS) volume PM sampler on quartz fiber or cellulose membrane filters for 24 h, which is in accordance with another standard method by CEN (EN 12341:2014), (ii) subsequent microwave digestion (MW) of PM-loaded filters using nitric acid ($HNO_3$) and hydrogen peroxide ($H_2O_2$), and (iii) analysis by inductively coupled plasma mass spectrometry (ICPMS) or graphite furnace atomic absorption spectrometry (GFAAS) (EN 14902:2005). The method is recommended for monitoring purposes in the European Union (Directive 2015/1480/EC) to obtain comparable results between different laboratories and to track the reduction of air pollutants ordered in Directive (EU) 2016/2284. Concentration ranges, target values and expected uncertainties are gathered in Table 1. Although this method is standardized only for As, Cd, Ni, and Pb, it is commonly used for the determination of other elements as well, although EN 14902:2005 does not guarantee accuracy for them; those results should be thus treated with caution.

As an alternative method, EDXRF was positively evaluated in the EU Scientific and Technical Research Report from 2011 [6], especially for source apportion purposes. However, EDXRF has not yet been classified as a standard method in EU, since some of the elements (*i.e.,* Cd and Cr) did not meet the European legislative and EMEP (Cooperative program for monitoring and evaluation of long-range transmission of air pollutants in Europe) requirements. The performance of EDXRF will be thus described in later parts of this manuscript.

### 2.2. *EPA (United states environmental protection agency)*

EPA describes 2 reference methods for the determination of Pb in airborne PM (EPA, 40 CFR Part 50): (i) determination of Pb in total suspended particles (TSP; particles <25–50 µm) by ICPMS (appendix G), and (ii) determination of Pb in $PM_{10}$ by EDXRF (appendix Q). According to the reference methods, the defined PM fraction (TSP or $PM_{10}$) is collected on (i) glass fiber, quartz, or polytetrafluoroethylene (PTFE) filters by a high-volume PM sampler or on (ii) PTFE filters by a low-volume sampler, every time for 24 h. In the case of TSP, Pb is then extracted from the sample by a heated ultrasonic bath using $HNO_3$ and hydrochloric acid (HCl) or with use of a heated block digestion using only $HNO_3$. The extract is measured by ICPMS. $PM_{10}$ sample, on the other hand, is directly analyzed by EDXRF, without any sample pretreatment step (EPA, 40 CFR Part 50). Similar to the CEN standard method, these procedures are only validated for Pb, although the prescribed analytical techniques in principle allow for multi-element analysis.

In addition, in "Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air" (EPA/625/R-96/010a), EPA also publishes detailed analytical procedures for the determination of (other) metals in PM with X-ray fluorescence (XRF), ICPMS, PIXE, neutron activation analysis (NAA), atomic absorption spectrometry (AA), and inductively coupled plasma spectrometry (ICP). Most of the described techniques have multi-element capabilities, however, those methods are only provided as a guidance to support regional, state and local regulatory agencies and will be described in the next section of this manuscript.

**Table 1**
Concentration ranges for the CEN method, target values and expected uncertainties.

| Element | Working range* | | Target value** [ng m$^{-3}$] | Expected uncertainties** [%] |
|---|---|---|---|---|
| | Lower limit [ng m$^{-3}$] | Upper limit [ng m$^{-3}$] | | |
| Pb | 1 | 4000 | 500 | 25 |
| Cd | 0.1 | 50 | 5 | 40 |
| As | 0.5 | 350 | 6 | 40 |
| Ni | 2 | 100 | 20 | 40 |

* EN14902:2005.
** EU Directive 2004/107/EC and 2008/50/EC.

## 3. Other methods used for PM elemental analysis

Monitoring of ambient air properties can be performed online or offline and PM elemental composition determination is no different. It can be done directly at a sampling site or the particles can be sampled on an appropriate carrier and transported to a facility where they are analyzed with a delay.

### 3.1. *Online measurement techniques*

Online analytical techniques are capable of measuring PM properties, or specifically its composition in real time. The resolution of sampling can range from a few minutes to a few hours and online measurements typically provide a course of changes in the atmosphere during the day. The main advantage of online measurement techniques is the obtained diurnal profile, which can be correlated with other relevant parameters, such as day-night conditions, temperature variation, sun radiation, traffic rush hours, *etc.*, but also the subsequent sample handling as a source of possible errors is avoided. As online instruments have the benefit of monitoring metal air pollutants in real-time, necessary warnings can be announced instantly, at a time of elevated levels of pollution and not only a few days later.

Currently, on-line elemental analysis is possible by XRF instruments only. One such example is the instrument developed specifically for in-situ determination of metals in $PM_{10}$, $PM_{2.5}$ or both in quasi-real-time (delay of one sample) [7]. Sampling is performed by an active deposition of PM on a filter tape with 15–240 min time resolution. After sampling, the sample is analyzed on-site, while the next sample is being simultaneously collected.

This instrument can determine more than 24 elements simultaneously (including As, Cd, Ni, Pb, Cr, Cu, Zn, and Hg, which have to be reported according to Directive (EU) 2016/2284) and is easily transportable [8,9]. However, the limitation of measuring compounds that are present in very low concentrations (often close to or below the limit of detection (LOD) especially for short sampling times) is hindering its wider and more routine use.

### 3.2. *Offline measurement techniques*

In many cases, such as for large-scale source apportionment studies, which are very common, offline methods for PM analysis are much more convenient and better accepted than online measurement techniques. For offline analysis, PM is usually collected on a filter medium and is analyzed later in a laboratory at a different location with various analytical techniques. In the field of air monitoring, off-line methods are convenient because other pollutants besides the elemental composition can be measured in the same sample by a combination of complementary techniques. Typical time resolution of offline samples is 24 h (daily measurements), although different time resolutions are also used for research purposes. With 24 h collected filters, between-day variations or changes in seasons can be studied. The advantage of such time resolution is that enough material is mostly collected, so that the measured concentrations are above LOD (at least true for most elements). The drawback, however, is that within-day variations cannot be observed.

#### 3.2.1. *Sample collection*

Elemental composition of ambient PM is most commonly determined off-line. Depending on a fraction of PM of interest, PM samplers or cascade impactors are used for collecting samples. PM samplers draw the air through a filter, which captures particles from the airstream. The size of particles deposited on a filter is determined by a sampling inlet (*e.g.,* cyclone or impactor) that eliminates particles larger than the specified cut-off size. In this way, $PM_{10}$ or $PM_{2.5}$ samples are collected. Moreover, a dichotomous PM sampler also exists, which separates coarse (2.5–10 μm) and fine (<2.5 μm) size fractions [10]. On the other hand, cascade impactors consist of multiple stages where particles of specific sizes are deposited based on their aerodynamic properties.

For PM sampling, different filter matrixes are used, from quartz and glass fiber filters to PTFE, cellulose fiber, polycarbonate filters, and others. The filter choice is usually associated with characteristics needed for subsequent analysis with specific analytical instruments.

### 3.2.2. *Off-line analysis*

Besides the already mentioned ICPMS and XRF, many other analytical methods also exist for the determination of the elemental composition of diverse samples; *e.g.,* ion-selective electrodes, stripping voltammetry, inductively coupled plasma optical emission spectrometry (ICP-OES), flame atomic absorption spectroscopy (FAAS), GFAAS, which have already been compared in previously published review papers [4,11,12]. In the past, however, there have been attempts to use many of those methods for the PM elemental analysis and their suitability for this kind of samples is briefly summarized below.

Methods such as ion-selective electrodes and stripping voltammetry are not commonly used in atmospheric sciences because they measure only metals in free ionic forms and not their total concentration, which results in underestimating the metal content in a sample. Moreover, electrochemical methods exhibit relatively high LODs, and are known for multiple interferences and some other systemic biases, which are hardly avoided in complex environmental samples.

Spectrometric methods such as FAAS and GFAAS cannot determine refractory metals (such as Mo, W, Ta, Cr, V) and can measure only one or a few elements at a time, resulting in a time-consuming work. Further, the LODs for FAAS and ICP-OES are at least 10–100 times higher than in the case of ICPMS, which is often too high for the desired trace metal determination in PM samples. Additionally, all these methods (including ICPMS) typically require samples in a liquid form, which means that for the analysis of airborne PM sample pre-treatment (usually with microwave digestion) is needed. A pre-treatment step introduces another bias to the method, especially regarding the recovery rates of target metals, dilutes the sample and consumes extra time of trained laboratory staff. Moreover, any additional sample handling can cause sample loss or contamination.

Consequently, in the recent years, more and more scientists strive to use analytical methods that can determine elemental composition of PM directly from a solid sample, circumventing the sample pre-treatment step. This eliminates dilution and additional error added to the measurement with it, and minimizes the possibility of contamination, which further complicates the analysis at trace level concentrations as are found in the atmosphere. Therefore, in the current paper, we pay special attention to solid-sample analytical techniques, such as XRF, PIXE, INAA, and LA-ICPMS. These methods are roughly compared in illustration in Fig. 2 and critically discussed in the remainder of the paper. All of them allow for the multi-element analysis, each of them having specific limitations.

Because of its simplicity, available portable instrument solutions, nondestructive nature and low cost, XRF is the most commonly used method for the determination of elemental composition among atmospheric scientists. Most widely used is EDXRF, which is also a reference method for air monitoring by EPA. Sometimes, other variations are also utilized for research purposes. Wavelength dispersive x-ray fluorescence (WDXRF) is not so popular for PM analysis since it normally uses high powers, which could embrittle the filter and alter particle morphology after exposure. Synchrotron radiation x-ray fluorescence (SRXRF), on the other hand, performs with a very high precision for heterogeneous and complex samples, but it requires synchrotron radiation as an excitation source, which makes its access very limited. In the TXRF variation, the spectral background is minimized (reduced background noise compared to XRF), excitation frequency of the elements is consequently increased and the sensitivity is improved [13].

PIXE and NAA are both nuclear analytical techniques and are thus of limited availability. Very qualified staff is also required to perform those analyses. INAA is the most commonly used NAA set-up because no chemical pre-treatment of a sample is needed prior to irradiation. However, the amount of sample needed for the analysis is bigger than for XRF, PIXE, or LA-ICPMS techniques.

In the case of LA-ICPMS, the analysis step is the same as in the conventional liquid-injection ICPMS utilized also in the above-mentioned standard methods, the only difference lies in the sample introduction system which is laser ablation instead of a liquid sampler. In contrast to the other methods just introduced, LA-ICPMS is a micro-destructive technique.

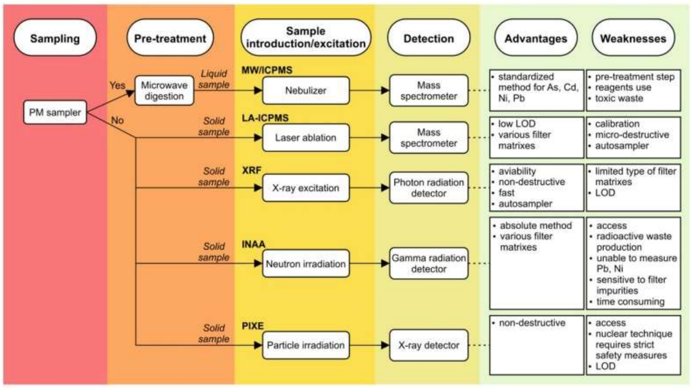

**Fig. 2.** Schematic comparison of the most suitable analytical methods for off-line PM analysis.

## 4. Comparison between MW/ICPMS and direct-analysis methods

### 4.1. Sample preparation

The conventional microwave digestion ICPMS (MW/ICPMS) analysis requires a sample in a liquid form, which is the greatest disadvantage of this method. Therefore, any solid sample (as is PM) needs to undergo a sample pre-treatment step with microwave digestion, where it is digested with concentrated acids. Problems that arise from such PM sample preparation are summarized below:

- The need for sample transformation into a liquid form introduces an additional step with a possibility of sample contamination. Reagents used for sample digestion must be high-purity, otherwise the contained impurities increase the background and LODs rise above the levels of trace elements in analyzed samples. As the usage of high-purity reagents complicates their production, it also raises the cost of analysis. Moreover, the used acids consequentially end up as toxic waste, which is non-negligible considering the necessity of monitoring on a global scale [14,15].
- The resulting sample digests are often not compatible with analytical instrumentation. Therefore, it is desired that concentrated acid digests are further diluted to avoid damage to ICPMS [16], which hinders trace elemental analysis due to instrumental LOD restrictions.
- In the case of quartz fiber filters, the filter matrix and therein caught PM particles are not completely digested by the prescribed standard methods. Furthermore, it is well known that not all PM components digest at the same rate, which puts multi-element determination under question [17,18]. One such example is mineral dust (specifically $SiO_2$), which completely digests only with hydrofluoric acid, complicating the analysis even further. When dealing with hydrofluoric acid very strict safety measurements and educated personnel are needed, additionally, boric acid has to be added before ICPMS analysis to form complex with free $F^-$ ions in the solution [15]. Furthermore, the use of hydrofluoric and boric acid contributes to the problems already described (*vide supra*) relating to LOD and toxic waste.
- Volatile elements (such as Hg) can be lost during microwave digestion.
- Possible explosion events due to overpressure in microwave vessels may lead to sample loss and destruction of laboratory equipment [19].
- This sample preparation step is time-consuming.

Solid sample techniques, on the other hand, simply require cutting a PM-on-a-filter sample to proper sizes, which are then fixed to the carrier (XRF, PIXE, LA-ICPMS) or fit into packages for irradiation (INAA). In this way, optimal analytical LODs are achieved and the possibility of sample contamination is minimized.

Microwave digestion, however, is sometimes also used prior to TXRF determination, so that the liquid sample can be dried out on a carrier to assure a smooth sample surface needed for the accurate measurement [13]. Although instrumental LOD is not challenged in this case and incomplete digestion does not result in systemic underestimation, all other drawbacks as listed above apply in the same manner. Moreover, Rovelli, et al. [20] propose dipping impactor samples into a solution of pure 3% glycerol diluted in ethanol/acetone 60/40 and evaporating the volatile solvents prior to LA-ICPMS analysis, to assure better fixation of particles on a medium. This was supposed to be a key step to avoid problematic sample loss during laser ablation as a consequence of the break-off of larger agglomerates from the PM spots, which did not reach ICPMS. However, this does not seem necessary for typical PM filter samples where PM is distributed all over the filter area and is not deposited discretely as on those impactor samples.

### 4.2. Number of elements determined and the concentration range

Elements of the greatest interest to atmospheric sciences are metals with known toxic effects and those elements that are good tracers for source apportionment studies. The CEN standardized MW/ICPMS method, however, targets the first group of analytes and certifies accurate determination of only four elements (As, Cd, Ni, Pb), although multi-element determination is theoretically possible with use of ICPMS. Consequently, digestion efficiency remains questionable for other elements and limits the number of elements to be accurately analyzed by the prescribed method. Nevertheless, the method is often used for multi-element analysis of ambient PM samples without evaluating the recoveries of other elements [17,18].

However, analysis of PM samples containing mineral dust (*e.g.* from Saharan dust events) is usually approached with care. The standardized MW/ICPMS method is not adequate to digest $SiO_2$, therefore, hydrofluoric acid has to be used for those analyses. The other surface analysing techniques do not require complete digestion and mineral dust does not present such issues. Mineral dust source has been identified in PM samples measured by EDXRF [21,22], TXRF with prior MW digestion [13], PIXE [23,24], and INAA [25].

All considered solid-sample techniques are also able to determine a wide range of elements in a single run. Since pre-treatment with microwave digestion is not needed, limitations in the number of elements accurately determined are solely due to instrumental restrictions and interferences. LA-ICPMS, XRF, and PIXE can all be used for the analysis of regulated As, Cd, Ni and Pb (plus many more elements), while INAA encounters some difficulties already in the determination of these four elements of interest. Namely, some elements exhibit insufficient nuclear reactions or even lack a nuclear reaction with target's nuclei (*e.g.,* Pb, Tl), while others are very close or below LOD in the case of PM samples (*e.g.,* Cd, Ni, Se); therefore, they are difficult or cannot be determined by INAA. This is a severe drawback, because monitoring of Cd, Ni, and Pb is required for regulatory purposes.

LA-ICPMS has the same measurement capabilities as liquid-injection ICPMS according to the standard methods; however, some difficulties have been reported in the determination of mercury (Hg) due to its volatile characteristics [26]. A pre-treatment with fixation of particles on a filter could be a solution to evaporation problems during the ablation, but this has not been verified to date.

Due to their poor positive ionization in a plasma, ICPMS is insensitive to halogens, which are most important in marine environments with high concentrations of chloride in ambient PM. Similar is true for lighter elements (*e.g.,* Na, Mg, Al, Si) in the case of XRF, due to their very low energy X-rays which are difficult to detect. In general, PIXE often encounters difficulties in the determination of trace elements due to the presence of high concentrations of major elements in a sample, especially those belonging to filter matrixes (*e.g.,* Si in the case of glass or quartz fiber filters). In the case of quartz filters, a thick Al-foil can be added to absorb X-ray photons of Si; however, this brings further problems in the determination of some other elements with low Z value (*i.e.,* Cl, K) [27].

In XRF, PIXE and INAA, interferences appear in a form of overlapping of spectral lines. In PIXE and some XRF techniques, high vacuum environment is preferred to prevent the interferences and beam energy loss when traveling through the air, but this can result in a selective loss of material, which is usually neglected [28]. On the other hand, in ICPMS, interferences arise from atomic or molecular ions with the same mass to charge ratio as the analyte of interest. In LA-ICPMS, a number of interferences diminish or even disappear compared to liquid-injection ICPMS due to the absence of solvents introduced into ICPMS [14]. Nischkauer, et al. [29] indeed avoided interferences from microwave digestion solvents by ablating a dried droplet of the digested sample, but this does not seem to be the best practice as it does not exploit the full potential of LA-ICPMS, which can be used without the sample pre-treatment step.

We summarize some of the identified interferences as reported in atmospherically relevant literature in Table 2. It must be emphasized that the table does not display all possible interferences, but only those listed in the reviewed articles where only a limited number of elements was targeted (mostly those relevant for PM pollution). Interferences related to instrument performance in general are out of scope of this paper.

Despite the wide detection possibilities of all considered instruments, the number of determined elements in PM samples can be reduced because of high background signals corresponding to the used filter matrix. Generally, the major constituents of filter matrixes (*e.g.,* Si in quartz or glass fiber filters) cannot be determined in PM by any of the techniques. The other background signals correspond to filter impurities and depend on the filter used.

The list of all elements, and corresponding LODs, measured in PM by different methods (MW/ICPMS, LA-ICPMS, INAA, PIXE, EDXRF, XRF) is reported in Table 3.

### 4.3. *Filter matrix*

Every method has its optimal filter matrix for the measurement of PM deposit. Some instruments are restricted to only one specific filter matrix, while others are more flexible and can use many different sample types. Especially in research, the desired filter matrixes are those which allow multiple complementary analyses for elemental and molecular characterization to be performed on the same sample; therefore, quartz fiber filters are regularly used. In this sense, the main limitation is usually the organic carbon/elemental carbon (OC/EC) thermo-optical analysis, where the filter needs to withstand up to 900 °C, which makes quartz the only viable choice. Moreover, the advantage of fiber filters is the ability to collect large PM masses. Žitnik, et al. [28] report on a successful collection of samples on quartz fiber filters with one-week resolution, while long-term sampling with membrane filters resulted in clogging which stopped the airflow through the filter after a single day of sampling in a port environment.

According to the standards, glass and quartz fiber filters, cellulose nitrate and cellulose acetate membrane filters and PTFE filters can be used for MW/ICPMS analysis, while only PTFE filters are suitable for standardized EDXRF measurements. INAA, on the other hand, does not prefer a certain filter type, as far as the contained impurities are below trace levels in analyzed samples.

In general, filter matrix impurities are one of the decisive properties for filter selection. Blank filter corrections are needed whenever the impurities in a blank filter contribute to the element signal. As PM mass deposited on a filter is much lower than the mass of the filter itself, variation in the level of filter impurities can even exceed actual concentrations of trace elements in the deposited PM. The level and type of impurities can differ between manufacturers and even between batches. Therefore, whenever the measured elements are present in a filter matrix, their determination in PM can be difficult. In general, quartz fiber filters contain more impurities than PTFE or polycarbonate filters [27, 28].

Important to understand is that surface techniques are much less sensitive to matrix impurities than MW/ICPMS and INAA. They target the filter surface where the majority of PM is deposited and do not measure bulk concentrations in a whole PM-on-a-filter sample. Still, fiber-based filters (quartz or glass) are not the optimal choice for any of the surface techniques, because the matrix is too thick and has an uneven surface; non-fabric-like matrixes of a membrane-type with pores are thus preferred (*e.g.,* PTFE, polycarbonate) [23,24,37]. Furthermore, in XRF and PIXE, membrane filters can be considered thin samples where the matrix effect is negligible [27]. Nevertheless, because of their wide acceptability, several attempts have been made to apply surface techniques to quartz fiber filter samples.

Quartz fiber samples have been analyzed with PIXE and compared with complementary PM samples on PTFE filters [23,27]. Corrections needed to be made for the filter thickness and Al absorber was used to suppress intensive Si peaks belonging to $SiO_2$ matrix (see also Section 4.2). Overall, PIXE elemental analysis of quartz fiber filters turned out to be less successful compared to PTFE filters: (i) approximately 2-times less elements can be determined, (ii) LODs are higher (1.5–3 times, except for the heavier elements, *i.e.,* Cu, Zn, Sr, and Pb) [27], (iii) accuracy and precision are worse. Hence, additional filter blank experiments are also required.

LA-ICPMS can use numerous types of filter matrixes, from cellulose membrane to Metricel membrane, PTFE, polycarbonate, quartz fiber filters, and others [20,30,37,45]. Smooth (membrane) matrixes make the ablation easier, because the structure of the filter is more homogeneous compared to fiber-based matrixes where fibers make the filter surface very uneven. Namely, for optimal ablation, the laser focus needs to be set at the top layer of the sample prior to analysis; there, the ablation will be most efficient. However, with the optimization of other laser ablation parameters (*e.g.,* dosage), the majority of PM can be ablated even when dealing with fiber-based matrixes, which makes glass and quartz fiber filters suitable for such analysis [26].

Of all considered techniques, TXRF has the strictest requirements for the sample type; the surface has to be smooth so that total reflection can be observed and preferably thin. The thickness of the sample material disrupts the total internal reflection at the surface, and leads to loss of fluorescence signals from the sample due to absorption in the sample layer. Different thin matrixes have been studied for PM analysis, such as polycarbonate [46,47] and PTFE membranes [48]. Quartz substrates are not well investigated. Bontempi, et al. [49] applied TXRF directly to PM on quartz fiber filters and reported difficulties in performing absolute quantification. To avoid the problems related to fiber filters, Fomba, et al. [13] subjected quartz filter samples to microwave digestion prior to the analysis and put a drop of digest on a smooth substrate, which was subsequently measured by TXRF. The advantage of this approach compared to MW/ICPMS is that particles do not have to be fully digested to obtain the required accuracy and sensitivity. However, it does not qualify for a direct-analysis method anymore. Another attempt was made to directly measure impactor PM samples on a polished quartz substrate greased with jelly organic paste, which was removed by cold-plasma ashing before the analysis; the analysis was feasible but of

**Table 2**
A list of reported interferences.

| Method | Measured nuclide | Interferences | Reference |
|---|---|---|---|
| LA-ICPMS | $^{78}Se$ | $^{40}Ar^{38}Ar^+$ and $^{38}Ar^{40}Ca^+$ | [26] |
| | $^{75}As$ | $^{40}Ar^{35}Cl$ | |
| | $^{52}Cr$ | $^{12}C^{40}Ar$ | [30] |
| | $^{53}Cr$ | $^{13}C^{40}Ar$ | |
| | $^{48}Ti$* | (Not reported) | [14] |
| | | $^{32}S^{16}O^+$, $^{34}S^{14}N^+$, $^{33}S^{15}N^+$, $^{14}N^{16}O^{18}O^+$, $^{14}N^{17}N^{2+}$, $^{12}C^{4+}$, $^{36}Ar^{12}C^+$ | [31] |
| | K | $^{38}Ar^1H^+$ | [32] |
| | m/z <40 | $ArH^+$, $ArN^+$, $ArO^+$ | |
| TXRF | Sb | Ca | [13] |
| SR TXRF | Si** | P and other low Z elements | [33] |
| INAA | $^{27}Mg$ | $^{56}Mn$ (and *vice versa*)*** | [34]<br>[35] |
| | $^{75}Se$ | $^{203}Hg$ | |
| | $^{235}U$ (fission products) | $^{95}Zr$, $^{95}Nb$, $^{97m}Nb$, $^{99}Mo$, $^{99m}Tc$, $^{139}Ba$, $^{140}La$, $^{141}Ce$, and $^{147}Nd$ | [35] |
| | Mg | Al**** | |
| | Al | Si (n,p) reaction | [34] |

* a different isotope ($^{49}Ti$) can also be measured.

** can be avoided with the choice of specific energy and measurement under vacuum.

*** should be measured at a specific cooling time since they have a different half-life.

**** $^{26}Mg(n,\gamma)^{27}Mg$ reaction competes with $^{27}Al(n,p)^{27}Mg$ (the amount of Al has to be determined for accurate determination of Mg).

**Table 3**
Limits of detection for different filter types and measuring methods in ng m$^{-3}$.

| | MW/ICPMS | | | LA-ICPMS | | | | INAA | | | PIXE | | EDXRF | | XRF | EDXRF-FP | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EPA * | Quartz fiber filter | Polycarbonate impactor foil | Quartz fiber filter | PTFE impactor foil | Polycarbonate impactor foil | Cellulose nitrate membrane filters | Quartz fiber filter | PTFE filter | Cellulose nitrate membrane filters | Quartz fiber filter | PTFE filter | PTFE filter | Polycarbonate filter | PTFE filter | Quartz fiber filter | Polycarbonate filter |
| Ag | 0.01 | | | | | | 0.00167 | | 0.04–0.06 | 0.2 | | 165.81 | | | | | |
| Al | 0.01 | | | | | | 1.67 | | 5–200 | 2 | | 16.25–20 | 5 | | 6–14 | | |
| Ar | | | | | | | | | 0.04 | | | | | | | | |
| As | 0.3 | 0.14 | | 0.06 | 0.019 | | 0.08 | 0.1 | 0.09–1 | 0.3 | | 5.42–15 | 0.8–3 | | 0.2 | | |
| Au | | | | | | | | | 0.09–1 | | | 14.44 | | | | | |
| Ba | 0.1 | | 0.06 | | | 0.003 | | | 2.3–5 | | | 13–22.57 | 0.5 | | | | |
| Be | 0.02 | 0.04 | | 0.01 | | | | | | | | | | | | | |
| Bi | | | | | | | | | | | | 16.85 | | | | | |
| Br | | | | | | | | | 0.04–0.5 | | 0.7 | 12.34–27 | 0.5–2 | 1.1 | 1 | | |
| Ca | | | | | | | 10.04 | | 200–231 | 60 | 9–15 | 4.9–8.12 | 2–18 | 18 | 9–60 | 31.5–67 | 193 |
| Cd | 0.02 | 0.02 | | 0.04 | | | 0.00335 | | 0.3–4.2 | | | 201.62 | | | | | |
| Ce | | | | | | | 0.00084 | | 0.05–9.2 | 0.3 | | 18.06 | | | | | |
| Cl | | | | | | | | | 9.2–100 | | 10 | 5–12.34 | 64 | 120 | 2–7 | | |
| Co | 0.01 | 0.12 | | 0.66 | | | 0.05 | | 0.01–0.4 | 0.1 | | 2.37–4.5 | 0.1 | | | | |
| Cr | 0.01 | | 0.1 | | | 0.03 | 0.33 | | 0.2–92.5 | 0.5 | 1.1–5.4 | 2.6–3.91 | 0.9–13 | 2.3 | 1 | 2.1–4.5 | 13 |
| Cs | | | | | | | | | 0.02 | | | 25.28 | | | | | |
| Cu | 0.01 | | 0.9 | | 0.009 | 0.03 | 11.72 | | 0.9 | 12 | 0.6 | 2.71–5.4 | 0.5–5 | 1 | 0.7–2 | 4.2–9.1 | 25.9 |
| Dy | | | | | | | | | 0.00001 | | | 9.63 | | | | | |
| Er | | | | | | | | | 0.2 | | | 8.73 | | | | | |
| Eu | | | | | | | | | 0.00041–0.01 | | | 10.53 | | | | | |
| F | | | | | | | | | 92.5 | | | | | | | | |
| Fe | | 2.35–15.28 | 1.6 | 1.92–2.3 | 0.37 | 0.06 | 2.51 | 39.54 | 50–4629 | 56 | 1.2–10 | 2.71–3.3 | 0.7–5 | 2 | 2.5–6 | 11–23.4 | 67 |
| Ga | | | | | | | | | | | | 3.61 | 0.1 | | | | |
| Gd | | | | | | | | | 9.2 | | | 10.23 | | | | | |
| Ge | | | | | | | | | | | | 4.21 | | | | | |
| Hf | | | | | | | | | 0.01–8.2 | | | 10.53 | | | | | |
| Hg | | | | | | | | | 0.02–0.9 | | | 14.44 | | | | | |
| Ho | | | | | | | | | 0.02 | | | 9.34 | | | | | |
| I | | | | | | | | | 0.1–5 | | | 29.19 | | | | | |
| In | | | | | | | | | 0.02 | | | 239.88 | | | | | |
| Ir | | | | | | | | | 0.0092 | | | 12.34 | | | | | |
| K | | | | 1.739 | | | 26.79 | 70.86 | 0.92–50 | 120 | 15–20 | 5.1–9.93 | 3–23 | 25 | 2–5 | 13.4–28.7 | 82.2 |
| Kr | | | | | | | | | 0.5 | | | | | | | | |
| La | | | | | | | | | 0.1–0.2 | | | 20.76 | | | | | |
| Lu | | | | | | | | | 0.0042 | | | 10.83 | | | | | |
| Mg | | | | | | | | | 50–231 | | | 18.66 | | | | | |
| Mn | 0.02 | 0.07–0.42 | 0.08 | 0.084–1.39 | 0.016 | 0.002 | 1.34 | 0.05 | 0.02–0.1 | 0.4 | 1.3–4.9 | 3–3.01 | 0.8–11 | 2.2 | 1–1.4 | 1.2–2.5 | 7.2 |
| Mo | 0.02 | | | | | | | | 1–5 | | | 57.17 | | | | | |
| Na | | | | | | | 39.33 | | 0.18–100 | 39 | | 28.28 | | | | | |
| Nb | | | | | | | | | 46 | | | 43.63 | | | | | |
| Nd | | | | | | | | | 1–9.2 | | | 15.05 | | | | | |
| Ni | 0.02 | | 0.04 | | 0.114 | 0.004 | 0.08 | | 1–1.8 | | 0.6 | 2.37–4.1 | 0.5–5.1 | 1.4 | 0.3 | 1.1–2.4 | 6.9 |
| Os | | | | | | | | | | | | 12.94 | | | | | |
| P | | | | | | | | | | | | 14.44 | | | 2 | | |
| Pb | 0.01 | 0.03 | 0.01 | 0.05 | 0.004 | 0.002 | 0.04 | | | | 2–11 | 16.85–29 | 0.5–2 | 1.3 | 1.8–2 | 3.8–8.1 | 23.1 |
| Pd | | | | | | | | | 0.09 | | | 134.21 | | | | | |
| Pm | | | | | | | | | | | | 12.64 | | | | | |
| Pr | | | | | | | | | 0.04 | | | 15.95 | | | | | |
| Pt | | | | | | | | | 1.8 | | | 13.54 | | | | | |

(continued on next page)

**Table 3** (*continued*)

| | MW/ICPMS | | | LA-ICPMS | | | | INAA | | | PIXE | | EDXRF | | XRF | EDXRF-FP | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EPA * | Quartz fiber filter | Polycarbonate impactor foil | Quartz fiber filter | PTFE impactor foil | Polycarbonate impactor foil | Cellulose nitrate membrane filters | Quartz fiber filter | PTFE filter | Cellulose nitrate membrane filters | Quartz fiber filter | PTFE filter | PTFE filter | Polycarbonate filter | PTFE filter | Quartz fiber filter | Polycarbonate filter |
| Rb | | | | | | | | | 1–18.5 | | | 17.75 | 1–3 | 1.1 | 0.7–1 | | |
| Re | | | | | | | | | 0.02 | | | 13.24 | | | | | |
| Rh | | | | | | | | | 0.0092 | | | 104.72 | | | | | |
| Ru | | | | | | | | | 0.9 | | | 89.37 | | | | | |
| S | | | | | | | | | | | 20 | 5.7–12.94 | 2 | 230 | 14–36 | 6.5–13.9 | 39.7 |
| Sb | 0.01 | 0.21 | | 0.17 | 0.019 | | 0.00697 | 0.02 | 0.2–0.4 | 0.1 | | 376.16 | | | | | |
| Sc | | | | | | | | | 0.003–0.09 | | | 4.8–7.82 | 2 | | | | |
| Se | 1.1 | 0.33 | | 0.02 | | | 0.05 | | 0.1–9.2 | 0.3 | | 6.32 | 0.6 | | | | |
| Si | | | | | | | | | | | | 8.9–14.14 | 3 | 2700 | 9–27 | | |
| Sm | | | | | | | | | 0.04 | | | 12.04 | | | | | |
| Sn | | | | | | | | | 9.2 | | | 272.64 | | | | | |
| Sr | | 0.24 | | 0.07 | | | | | 0.4–0.4 | | 1–13 | 23.17–28 | 0.5–3 | 1.1 | 1–1.3 | | |
| Ta | | | | | | | | | 0.005–4.2 | | | 10.83 | | | | | |
| Tb | | | | | | | | | 0.01–2.3 | | | 9.34 | | | | | |
| Tc | | | | | | | | | | | | 73.12 | | | | | |
| Te | | | | | | | | | 4.6 | | | 30.99 | | | | | |
| Th | 0.01 | | | | | | | | 0.1–3.2 | | | 33.7 | | | | | |
| Ti | | | | | | | 0.08 | | 4.6–200 | 17 | 3–5.7 | 3.1–6.62 | 1–22 | 7.1 | 1 | 4.7–10 | 28.7 |
| Tl | 0.01 | | | | | | | | | | | 16.55 | | | | | |
| Tm | | | | | | | | | | | | 10.23 | | | | | |
| U | 0.01 | | | | | | | | 0.03–0.2 | | | 43.94 | | | | | |
| V | 0.01 | 0.03 | | 0.01 | 0.003 | | 0.01 | 0.21 | 0.04–1 | 0.2 | 1.8–5.4 | 2.4–5.42 | 1 | 4.6 | 0.1 | 1.49–3.2 | 9.1 |
| W | | | | | | | 0.00084 | | 0.01–0.09 | 0.3 | | 12.04 | | | | | |
| Y | | | | | | | | | 0.09 | | | 28.59 | | | | | |
| Yb | | | | | | | | | 0.01–0.2 | | | 10.53 | | | | | |
| Zn | 0.04 | 0.6–6.94 | 0.5 | 0.49–1.85 | 0.16 | 0.03 | 2.51 | 1.43 | 0.5–9.2 | 6 | 0.5–4.2 | 3.61–6.7 | 0.5–4 | 1.1 | 0.7–12 | 2.7–5.7 | 16.2 |
| Zr | | | | | | | | | 92.6 | | | 35.51 | | | | | |
| Refs. | ** | [36]<br>[26] | [15] | [36]<br>[26] | [37] | [15] | [38] | [26] | **<br>[10] | [38] | [27]<br>[28] | ** [27] | [39] [40]<br>[41] | [42] | [43] | [44] | [44] |

* Filter information not found.

** EPA/625/R-96/010a.

very limited use (*i.e.*, short sampling times), since the layer of deposited PM had to be very thin [13,50]. In fact, it is difficult to control the thickness of deposited PM in impactor collected samples for accurate TXRF measurement, whereas multiple layers of PM on a carrier hinder the analysis.

### 4.4. Sample throughput

Sample introduction is an important part of every analysis and becomes a critical step especially when it comes to biological or field samples. Whenever the collected sample is not analyzed as a whole, the part of a sample that is taken for analysis can importantly influence the accuracy of the measurement and the time of analysis. This is also the case with PM deposit on filter samples, homogeneity of which is often questioned. Brown, et al. [51] recognized that whenever dealing with solid samples, homogeneity assessment is a very important part of method development, but is often overlooked which can lead to errors and inaccurate analysis results. A researcher must assure that a small part of a filter taken for analysis (so called sub-sample) is representative of the whole filter, which intrinsically applies to all types of samples considered in this paper.

Homogeneity of PM samples is mostly influenced by unique composition of every individual particle in PM mass. However, only a part of a collected sample is usually analyzed for its elemental composition; to spare sample for analysis with other complementary techniques, because of instrumental constraints, and sometimes also to shorten the time of analysis, which can depend on the size of a subsample. To minimize the sampling error, a sub-sample large enough to be representative of the PM population must always be taken.

In the case of the standard MW/ICPMS methods, sample pretreatment step is a bottleneck, whereas the time of analysis is not connected with the sample size. According to the CEN method (EN14902:2005), sample preparation for liquid-injection ICPMS takes about 3 h (preparation and digestion program – 1 h, cooling time – 30 min, cleaning the vessels – 1.5 h) and is a laborious work, its throughput being limited by the number of available staff and microwave performance (number of vessels per run, cooling time *etc.*). Moreover, the sample amount that can be digested in a vessel is also limited and influences the LOD.

With LA-ICPMS, the measurement is performed pixel by pixel, so the analysis time is directly connected with the size of the analyzed filter area. The times of analysis can additionally differ due to selected scanning parameters, which are intrinsically connected with the used instrumental setup. In one of the early publications, Wang, et al. [14] estimated the analysis time to be 10 min per sample, however, after a thorough sample homogeneity examination [26], the analysis time approaching 30 min per sample was achieved.

For XRF and PIXE, a wide analysis time range has been reported due to different measurement needs (*e.g.,* number of analyzed elements) and parameters used. For EDXRF, the reported analysis times are from 15−167 min per sample [6,40,44]. According to EPA, approximately 4 h of machine time are required for 44 analyzed elements by utilizing all seven fluoresces and 15 samples can be measured at a time (EPA/625/R-96/010a). For PIXE, the required irradiation time for a 5 mm diameter spot was reported to be 25–35 min [27], whereas the measurement times of 30 min per sample [28] and 1 h per sample (90 s bombarding; 2 $mm^2$ spot size) [23] have also been reported. For TXRF an approximate acquisition time is in a range of a few minutes [49], moreover, with appropriate autosampler a sample throughput can be expedited (*e.g.* with autosampler that can process 90 samples at a time, the processing time is brought down to 20 min).

Although INAA is one of the most sensitive methods, it is also the most time-consuming. The analysis can be divided into 3 parts: (i) the irradiation time, (ii) the cooling time that is based on the element half-life, and (iii) the measurement time. The cooling period is the longest and can last for even more than 20 days [10]. A set of samples can be irradiated and cooled at the same time, but every sample needs its own detector, which is often a bottleneck.

It is worth noting at this point that besides sample analysis, measurement of calibration standards also contributes to the time of analysis. Calibration procedures are elaborated in the next chapter.

### 4.5. Calibration

When discussing calibration, the techniques can be divided into two groups: (i) techniques that require certified reference material (CRM) and (ii) techniques that do not require CRM for quantification.

The standard MW/ICPMS method belongs to the first group and needs to be calibrated every measurement round. The easy calibration is the advantage of the standard method, since liquid standards are readily available.

To ensure the same ablation rate in samples and standards, hence correct calibration, LA-ICPMS requires matrix-matched standards for calibration. The number of suitable commercially available standards (PM deposited on a suitable filter) are very limited. Commercially available standard reference material (SRM) 2783 from the National Institute of Standards and Technology (NIST) proved to be a good calibration standard for PM samples on polycarbonate filters [37]. However, it cannot be used for other filter types, for which different approaches have been proposed. Liquid standards spiked to different substrates [14,20,36,52] or dust standards (*e.g.,* NIST SRM 1684a) in a form of pellets or deposited on a substrate [30,32] were used. Nevertheless, most of these approaches cope with difficulties due to non-homogeneity and reproducibility. Therefore, Ogrizek, et al. [26] have recently used a field sample for calibration purposes; the sample was first calibrated by INAA, which does not require specific CRM for calibration, and used as a standard later on in the analysis.

XRF methods and PIXE are mostly calibrated by commercial thin-film standards. Most commonly used are single element filter standards from Micromatter [23,24,28,42]. Such calibration is suitable for sample matrixes behaving as thin samples. When using quartz filters, however, special correction calculations need to be applied. In EDXRF, calibration is a very complex and time-consuming procedure, in which sensitivity and the magnitude of interferences are defined. Calibration can thus last for two weeks, but fortunately it needs to be performed annually or when significant instrument repairs or changes occur (EPA/625/R-96/010a). EDXRF can also be coupled with fundamental parameter quantification technique (EDXRF-FP), which qualifies for a standardless technique. In this case, quantification is based on modeling and theoretical calculations, sample thickness being one of the input parameters. FP quantification is satisfactory for most of the elements, except for Mn, Pb, and Ni [6,44].

The only true representative of the second group of techniques is an absolute method INAA. For the application of $k_0$-INAA, a comparator Al-0.1 % Au standard alloy is usually measured together with samples [26, 53]. Because it does not need specific matrix-matched standards for calibration, it can be very useful in the development of new standard materials (note the attempt by Ogrizek, et al. [26]).

### 4.6. LOD, accuracy, precision

#### 4.6.1. Accuracy

Accuracy of a method is usually determined by measuring a reference material and comparing the determined values to certified values. For surface techniques, a matrix-matched standard is advised for the assessment of accuracy. NIST SRM 2783 (air particulate on polycarbonate filter membrane) is often used to assess the accuracy of a method for samples with similar matrix properties; the reported deviations are below 15 % for PIXE [24], ± 10 % for PIXE and INAA [54], and ± 10 % for EDXRF (EPA/625/R-96/010a). Since no CRM of certified element concentrations on a quartz filter exists, it is difficult to assess the accuracy of those types of samples.

In the field of atmospheric chemistry, it is not unusual to work with relatively high accuracy deviations, which is due to the nature of collected samples (inhomogeneity and trace concentrations). According to Directive 2004/107/EC, the accuracy of the standard MW/ICPMS method is within 40 % for As, Cd, and Ni.

### 4.6.2. Precision

Measurement precision is mostly assessed by repetitive measurements and is expressed as the relative standard deviation (RSD). Precision can, among others, be influenced by sample heterogeneity (this can be minimized by measuring large enough sample area) and measured concentrations (often larger variations at trace element concentrations).

In general, ICPMS is a very precise instrument (RSD $<$ 10 %) [18], however, the bottleneck here is again the pre-treatment step, where different recoveries obtained in microwave digestion add to the variation when measuring different PM matrixes (EPA/625/R-96/010a).

The precision of surface techniques is usually not as good as for the ideally homogenous samples, mostly due to the heterogenic composition of PM, uneven surface, and some concentrations close to LOD. Nevertheless, all the reported alternative analysis methods to MW/ICPMS; surface analysis methods (PIXE, EDXRF, SR-XRF, LA-ICPMS) and INAA generally exhibit good precision, bellow 15 %. Higher RSDs were reported for measuring quartz fiber filter matrixes (up to 75 %) and for some trace elements in PTFE filters ($<$ 50 %) with PIXE [27]. Precision for PTFE filters were also reported for LA-ICPMS ($<$ 30 %) [14] and EDXRF ($<$ 10 %) [55], no precision was reported for other techniques for the analysis of quartz fiber filters in the reviewed articles; the reported precisions are summarized in Table 4.

Brown, et al. [30] reported high RSD (10–100 %) for the LA-ICPMS analysis of impactor spots on Maricel membrane filters. Their repeatability was highly influenced by liberating large particles from a sample during the ablation process, which resulted in signal spikes and elevated RSD (besides material loss as already discussed). The addition of a small in-line filter device (*i.e.,* glass wool) in the carrier gas line, filtering out larger particles formed during the ablation, improved the repeatability of the analysis (5 % RSD). This, however, could result in a selective loss of some analytes and particle sizes. To reduce RSD, signal spike removal prior to raw data analysis has also been used by Robinson, et al. [37] and Ogrizek, et al. [26], who did not attribute acquired spikes to the just described ablation phenomenon. Their spikes were presumably relatively clean nanoparticles consisting of high proportions of metals, which largely contributed to the determined RSD (precision), but not to the average concentration of the element in a sample (accuracy) [26]. For example, in the case of As, the removal of spikes resulted in 3 % reduction of the mean (max 9 % was estimated for other elements) and improved RSD for 82 %, improving also repeatability of the measurement.

### 4.6.3. LOD

LOD or method detection limit (MDL) is one of the most important parameters in chemical analysis and is especially important in samples where concentrations are low. It is difficult to compare LODs from different reports since there is no generally accepted formula for its estimation and different strategies for its calculation are used. However, LOD assessment is most commonly based on the calculated standard deviation (SD) of repeated measurements of blank or field blank filter impurities (*e.g.,* 3 × SD) [36,55].

In atmospheric chemistry, the results are usually expressed in units of mass per volume of air (μg m$^{-3}$ or ng m$^{-3}$), which additionally complicates comparison between different techniques. Without the information about the volume of sampled air, instrumental LODs cannot be compared. More useful would be concentrations expressed in a form of mass of element per PM mass or filter area (μg g$^{-1}$ or μg cm$^{-2}$), but those are rarely reported. Another argument as to why μg m$^{-3}$ are not the units of choice is that LODs are mostly based on blank filter measurements, which by definition did not have any air drawn through (air volume is zero). LODs in ng m$^{-3}$ as reported in different papers for the different methods are gathered in Table 3.

### 4.7. Availability and costs

When building a monitoring network as well as in research, technique capabilities and performance are often compared with the initial investment (*i.e.,* price of an instrument) and cost of analysis, which involves ease of instrument operation (*i.e.* how trained staff is required) and waste management.

EDXRF is the cheapest instrument taken in consideration, ranging from a few tens to hundred thousands of euros (depending on the instrument capabilities; from simple analysis to more complicated image analysis). The price of MW/ICPMS and LA-ICPMS is in the range of more expensive EDXRF instruments (a few hundred thousand euros), microwave being a few times cheaper than the current LA system used, although less advanced laser systems might be appropriate (*e.g.* 213 nm instead of 193 nm lasers and the price would be reduced by half). PIXE and INAA are considered in the highest rank of investment costs, where PIXE system costs above a million of euros and INAA even requires a special facility, specifically designed for the reactor.

As already mentioned, EDXRF is an inexpensive [42] and nondestructive method, therefore even standards and costly reference materials can be used multiple times. Manufactures have already optimized it specifically for PM filter analysis (Thermo Fisher Scientific Inc., Malvern Panalytical Ltd), which probably makes it the technique of choice for new environmental/atmospheric laboratories. The instrument is benchtop size and easy to use [42], portable solute ions are also available and only electricity is needed for its operation. The build-in calibration approach additionally facilitates work in field campaigns. An

**Table 4**
Reported precisions for different methods and filter matrixes.

| Method | Filter matrix | Elements | Precision | Reference |
|---|---|---|---|---|
| PIXE | PTFE filter | major constituents (Al, Si, S, K, Ca, Fe, Zn) | 1–15 % | [27] |
| | | other elements (*i.e.*, Ti, V, Cr) | 20–50 % | |
| | quartz fiber filters | K, Fe and Zn | 20–50 % | |
| | | other elements (*i.e.*, Ca, Ti, V, Cr, Mn) | 35–75 % | |
| | Nucleopore, polycarbonate | 10 elements (Al, Si, K, Ti, Mn, Fe, Ni, Cu, Zn, Pb) | 5–15 %, | [54]<br>[56] |
| INAA | Nucleopore, polycarbonate | 10 elements (Na, K, Sc, Cr, Fe, As, Br, La, Sb, Sm) | 5–15 %, | [54]<br>[56] |
| EDXRF | PTFE | 12 elements (Se, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb) | <10 % (duplicate samples) | [55] |
| SR-XRF | polycarbonate | 10 elements (Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn) | <10 % (triplicates, 3 different positions) | [57] |
| | polycarbonate | 8 elements (Cr, Mn, Fe, Ni, Cu, Zn, Ba, Pb) | <5–10 % (RSD between 4 impactor spots) | [15] |
| LA-ICPMS | PTFE membrane | 21 elements (Na, Mg, Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, Ba) | < 15 % (RSD, 7 repeated shots; 1 mm diameter) | [14] |
| | | Al, Ti, Pb | < 20 % | |
| | | Sr | < 30 % | |

**Table 5**
A summary of comparison of LA-ICPMS, XRF, PIXE, and INAA methods with MW/ICPMS.

| | MW/ICPMS | LA-ICPMS | XRF | PIXE | INAA |
|---|---|---|---|---|---|
| **Sample pre-treatment** | Yes | No | No | No | No |
| **Multi-element** | Yes/No*<br>*Certified only for Pb, Cd, Ni, As (restriction = MW) | Yes<br>(poor sensitivity to halogens) | Yes<br>(poor sensitivity to light elements) | Yes<br>(difficulties with high conc. matrix signals) | Yes<br>(poor sensitivity to Pb and others) |
| **Matrix**<br>**-thin films: PTFE, cellulose, polycarbonate** | Yes | Yes | Yes | Yes | Yes |
| **-quartz filter** | Yes<br>(but incomplete digestion) | Yes | with modification | Yes | Yes |
| **Interferences** | Ions with the same m/z value | Ions with the same m/z value | Overlapping spectral lines | Overlapping spectral lines | Overlapping spectral lines |
| **LOD** | Low/Moderate*<br>*sample dilution | Low | Moderate | Moderate | Low |
| **Accuracy** | Good/Medium*<br>*MW digestion step | Good | Good | Good | Good |
| **Time** | Moderate | Fast | Fast | Fast | Slow |
| **Calibration** | Liquid standards | Matrix matched standards | Thin-film standards or FP | Thin-film standards | No standard |
| **Hazard** | Dangerous chemicals & toxic waste | No toxic waste | No toxic waste | Particle radiation | Nuclear radiation & radioactive waste |
| **Sample amount** | Medium | Small | Small | Small | Medium |
| **Sample destruction** | Destructive | Micro-destructive | Nondestructive | Nondestructive | Nondestructive (but radioactive and damaged) |

auto-sampler allows for the analysis of many samples without the continuous control of laboratory staff.

MW/ICPMS is one of the most widely used analytical techniques in routine air quality monitoring and the required infrastructure consists of two separate instruments: microwave and ICPMS. For PM analysis, high-purity solvents for sample digestion (which also produce toxic waste at the end of analysis), high-purity gases for instrument operation, and standards for quantitation are needed.

In the case of LA-ICPMS, microwave is simply replaced by somehow more expensive and advanced LA system. Although the initial investment may seem substantial, operation/usage costs are drastically reduced; it only requires electricity and carrier gases for ICPMS (same as above) and circumvents solvent consumption and staff for wet laboratory work. Both techniques, however, require educated personnel for instrument operation and data analysis. Automatization facilitates any laboratory analysis and usually improves throughput. Autosamplers for liquid-injection ICPMS systems already exist, while there are specially developed autosamplers for LA-ICPMS on the market, but none is suitable for PM filter analysis without modification.

PIXE and NAA are both nuclear techniques and require an accelerator for particle beam generation or a nuclear reactor for the source of irradiation, respectively. The techniques cannot be set in every laboratory, but rather special facilities are required for the setup and operation. These are certainly not easily accessible. All nuclear techniques have specific hazards, therefore strict safety measures have to be taken to protect staff and the surrounding environment. Similar can be applied also to SRXRF, which requires a synchrotron source.

### *4.8. Waste management*

Production of toxic waste cannot be considered non-negligible especially when it comes to everyday monitoring on a global scale. Only in Europe, around 2900 official $PM_{10}$ monitoring sites have been reported in 2017 [58], collecting daily samples for the analysis. If all of those stations were determining elemental concentrations according to EN14902:2005, millions of liters of concentrated nitric acid would be used and end up as toxic waste per month. As we perform air quality monitoring to protect the environment in the long run, concomitant environmental pollution should be brought to a minimum.

Toxic acid waste is not produced where PM analysis is performed directly from a solid sample; *i.e.* XRF, PIXE, and LA-ICPMS. NAA also does not use toxic solvents; however, the irradiated samples are radioactive, turning them into radioactive waste after the analysis.

Except for ICPMS techniques, all others are theoretically nondestructive methods, which means that the same sample can be analyzed by multiple techniques. However, samples taken for INAA are not suitable for subsequent surface analysis due to the loss of original shape while being packed in a container for irradiation. Additionally, the sample remains radioactive for a while and cannot be reused within a reasonable time.

### *4.9. Performance*

We summarize the main characteristics of methods that are discussed in this review paper in Table 5.

However, the most realistic differences between methods are obtained if the same samples are analyzed with all or several methods under comparison. Brown, et al. [59] compared the standard MW/ICPMS method (EN14902:2005) to LA-ICPMS and EDXRF. They concluded that both solid-sample techniques exhibit low systematic bias. LA-ICPMS was unable to determine Cr, presumably due to interferences and high blank concentrations, but did provide additional information on other metals (*e.g.*, V, Fe) compared to the standard MW/ICPMS method. Other than a few elements, no significant difference was observed between EDXRF or LA-ICPMS and MW/ICPMS. However, according to Brown, et al. [59], improvements in repeatability and calibration for both EDXRF and LA-ICPMS would be beneficial. LA-ICPMS was also compared to high pressure bomb acidic digestion/ICPMS and proved to be more sensitive for many low-level elements [14].

Another comparison where the same PM sample was measured by MW/ICP-MS, LA-ICPMS, and $k_0$-INAA was made by Ogrizek, et al. [26]. The comparison was done on seven elements (As, Fe, K, Mn, Sb, V, and Zn), since those are the elements that could be determined by $k_0$-INAA. Statistically significant difference was observed for MW/ICPMS *vs.* LA-ICPMS and MW/ICPMS *vs.* $k_0$-INAA for As, Fe, and V, presumably due to incomplete digestion in MW/ICPMS. A comparison between LA-ICPMS and $k_0$-INAA did not show any significant difference, but it should be noted that the calibration for LA-ICPMS was based on $k_0$-INAA results; therefore, this comparison is not completely independent. LA-ICPMS was able to determine 12 more elements in the samples than $k_0$-INAA (*i.e.,* Al, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sn, and Tl), because $k_0$-INAA is more sensitive to filter matrix impurities and has difficulties in the determination of some of the elements in interest (*e.g.,* Pb).

PIXE and $k_0$-INAA have also been compared based on three elements measured in the same PM samples. K and Fe were in good agreement, while the results for Zn were worse, probably due to its low concentration and consequently more heterogeneous distribution on the filters [53].

## 5. Future PERSPECTIVE

The currently established standard methods were published in 2005 (CEN: EN14902:2005) and 2016 (EPA: 40 CFR Part 50, Appendix G and Q) in EU and US, respectively. In the last 15 years, no changes have been implemented into EN14902 protocol and no drastic advances in MW/ICPMS analysis have been published in the field of atmospheric chemistry. So it seems that the development of MW/ICPMS method has reached its limit and no radical advances are expected in near future. Despite its drawbacks discussed in this review paper, MW/ICPMS performs successfully for the needs of air quality monitoring (current requirements: Pb, As, Cd, and Ni); however, it can cause problems if only used periodically (as in research). Moreover, new elements are expected to be regulated in near future, which will challenge the current standards.

Scientific progress is providing more and new information about the toxicity of trace elements in ambient PM, which are expected to be included in updated regulations and standards (Directive (EU) 2016/2284). We can expect that multi-element analysis will be required for any PM determination in the future, which is already the case if one wants to successfully apply source apportionment models and identify pollution sources. Furthermore, in the past years, the trend has shifted towards sustainable or eco-friendly lifestyle, and more and more people strive towards minimizing the pollution and anthropogenic impacts to the environment, and so the awareness of the need for green analytical techniques is also increasing.

The considered solid-sample techniques (XRF, PIXE, LA-ICPMS, INAA) are essentially all multi-element techniques with no or minor need for sample pre-treatment, however these all have their own advantages and disadvantages. Quartz fiber filters, which can be additionally used for regulated polycyclic aromatic hydrocarbons (and other organic pollutants) determination and OC/EC analysis, still present a challenge for most of them. As INAA and PIXE are not easily affordable, they are thus not the first choice for routine air quality monitoring purposes. More promising methods for routine analyses are XRF and LA-ICPMS. EDXRF is the preferred method among XRF variations, because of the simplicity of use, accessibility, and customization for measuring PM samples (both WDXRF and SR-XRF need vacuum environment for operation, SR-XRF additionally requires synchrotron radiation source, and TXRF requires smooth and thin samples, which are difficult to achieve in PM samples analysis). EDXRF has already been established as a standard method for the determination of Pb by EPA and the manufacturers have provided simple and user-friendly set-ups with an autosampler specially adjusted for PM samples on thin film filters (*e.g.,* polycarbonate, PTFE). On the other hand, LA-ICPMS has not been as widely used for the determination of PM as EDXRF; because the methods have only recently been developed. Although LA-ICPMS has been successfully applied to many different filter types, the absence of suitable certified matrix-matched standards is momentarily a big disadvantage. Moreover, if the method is taken for validation for air quality monitoring purposes, a proper autosampler, customized for PM filters would also be required. However, autosamplers for other type of samples already exist and with minimal transformation they could be suitable for PM filter samples.

Although EDXRF is slowly making its way into environment agencies, it is currently standardized only for Pb. However, it has already been proposed as an alternative method for other elements determination as well. LA-ICPMS has the potential to follow the EDXRF course, after some additional development. Its advantage to EDXRF is the possibility to analyze PM deposited on quartz fiber filters, which are most versatile and could circumvent additional air sampling exclusively for the determination of PM elemental composition. On the other hand, EDXRF is the only reported technique available for on-line monitoring so far, which allows that sampling and analysis are done simultaneously at a location. It seems reasonable that especially these two techniques are evaluated further and possibly standardized for the element determination in PM, and slowly replace the currently well-established MW/ICPMS method which is laborious and incriminating to the environment.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

[1] F. Karagulian, C.A. Belis, C.F.C. Dora, A.M. Prüss-Ustün, S. Bonjour, H. Adair-Rohani, M. Amann, Contributions to cities' ambient particulate matter (PM): a systematic review of local source contributions at global level, Atmos. Environ. 120 (2015) 475–483.

[2] J. Lelieveld, J.S. Evans, M. Fnais, D. Giannadaki, A. Pozzer, The contribution of outdoor air pollution sources to premature mortality on a global scale, Nature 525 (7569) (2015) 367–371.

[3] C.A. Belis, D. Pernigotti, G. Pirovano, O. Favez, J.L. Jaffrezo, J. Kuenen, H.D. van Der Gon, M. Reizer, V. Riffault, L.Y. Alleman, M. Almeida, F. Amato, A. Angyal, G. Argyropoulos, S. Bande, I. Beslic, J.L. Besombes, M.C. Bove, P. Brotto, G. Calori, D. Cesari, C. Colombi, D. Contini, G. De Gennaro, A. Di Gilio, E. Diapouli, I. El Haddad, H. Elbern, K. Eleftheriadis, J. Ferreira, M.G. Vivanco, S. Gilardoni, B. Golly, S. Hellebust, P.K. Hopke, Y. Izadmanesh, H. Jorquera, K. Krajsek, R. Kranenburg, P. Lazzeri, F. Lenartz, F. Lucarelli, K. Maciejewska, A. Manders, M. Manousakas, M. Masiol, M. Mircea, D. Mooibroek, S. Nava, D. Oliveira, M. Paglione, M. Pandolfi, M. Perrone, E. Petralia, A. Pietrodangelo, S. Pillon, P. Pokorna, P. Prati, D. Salameh, C. Samara, L. Samek, D. Saraga, S. Sauvage, M. Schaap, F. Scotto, K. Sega, G. Siour, R. Tauler, G. Valli, R. Vecchi, E. Venturini, M. Vestenius, A. Waked, E. Yubero, Evaluation of receptor and chemical transport models for PM10 source apportionment, Atmos. Environ-X 5 (2020) 23.

[4] E.S. Galvao, J.M. Santos, A.T. Lima, N.C. Reis, M.T.D. Orlando, R.M. Stuetz, Trends in analytical techniques applied to particulate matter characterization: a critical review of fundaments and applications, Chemosphere 199 (2018) 546–568.

[5] B.R. Bzdek, M.R. Pennington, M.V. Johnston, Single particle chemical analysis of ambient ultrafine aerosol: a review, J. Aerosol Sci. 52 (2012) 109–120.

[6] S. Yatkin, M. Gerboles, A. Borowiak, G. Tanet, V. Pedroni, R. Passarella, F. Lagler, Evaluation of EDXRF for the determination of elements in PM10 filters, EUR 24983 EN, publication office of the european union, Luxemburg (2011).

[7] M. Furger, P. Rai, J.G. Slowik, J. Cao, S. Visser, U. Baltensperger, A.S.H. Prévôt, Automated alternating sampling of PM10 and PM2.5 with an online XRF spectrometer, Atmos. Environ. X 5 (2020).

[8] M. Furger, M.C. Minguillón, V. Yadav, J.G. Slowik, C. Hüglin, R. Fröhlich, K. Petterson, U. Baltensperger, A.S.H. Prévôt, Elemental composition of ambient aerosols measured with high temporal resolution using an online XRF spectrometer, Atmos. Meas. Tech. 10 (6) (2017) 16.

[9] A.H. Tremper, A. Font, M. Priestman, S.H. Hamad, T.C. Chung, A. Pribadi, R.J. C. Brown, S.L. Goddard, N. Grassineau, K. Petterson, F.J. Kelly, D.C. Green, Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols, Atmos. Meas. Tech. 11 (6) (2018) 3541–3557.

[10] P. Avino, G. Capannesi, F. Lopez, A. Rosada, Determination of interesting toxicological elements in PM2.5 by neutron and photon activation analysis, Transfus. Apher. Sci. (2013) 8.

[11] R.J.C. Brown, M.J.T. Milton, Analytical techniques for trace element analysis: an overview, Trac-Trends Anal. Chem. 24 (3) (2005) 266–274.

[12] S.C. Wilschefski, M.R. Baxter, Inductively coupled plasma mass spectrometry: introduction to analytical aspects, Clin. Biochem. Rev. 40 (3) (2019) 115–133.

[13] K.W. Fomba, N. Deabji, S.E. Barcha, I. Ouchen, E. Elbaramoussi, R.C. El Moursli, M. Harnafi, S. El Hajjaji, A. Mellouki, H. Herrmann, Application of TXRF in monitoring trace metals in particulate matter and cloud water, Atmos. Meas. Tech. 13 (9) (2020) 4773–4790.

[14] C.F. Wang, S.L. Jeng, C.C. Lin, P.C. Chiang, Preparation of airborne particulate standards on PTFE membrane filter for laser ablation inductively coupled plasma mass spectrometry, Anal. Chim. Acta 368 (1-2) (1998) 11–19.

[15] S. Rovelli, W. Nischkauer, D.M. Cavallo, A. Limbeck, Multi-element analysis of size-segregated fine and ultrafine particulate via Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry, Anal. Chim. Acta 1043 (2018) 11–19.

[16] R. Thomas, Practical Guide to ICP-MS, Marcel Dekker, Inc., 2004.

[17] K. Swami, C.D. Judd, J. Orsini, K.X. Yang, L. Husain, Microwave assisted digestion of atmospheric aerosol samples followed by inductively coupled plasma mass spectrometry determination of trace elements, Fresenius J. Anal. Chem. 369 (1) (2001) 63–70.

[18] J. Aldabe, C. Santamaría, D. Elustondo, E. Lasheras, J.M. Santamaría, Application of microwave digestion and ICP-MS to simultaneous analysis of major and trace elements in aerosol samples collected on quartz filters, Anal. Methods 5 (2) (2013) 554–559.

[19] M. Gerboles, D. Buzica, Intercomparison exercise for heavy metals in PM10, EUR 23219 EN, office for official publications of the European communities, Luxembourg (2008).

[20] S. Rovelli, A. Cattaneo, W. Nischkauer, F. Borghi, A. Spinazze, M. Keller, D. Campagnolo, A. Limbeck, D.M. Cavallo, Toxic trace metals in size-segregated fine particulate matter: mass concentration, respiratory deposition, and risk assessment, Environ. Pollut. 266 (2020) 10.

[21] C. Perrino, M. Catrambone, S. Canepari, Chemical composition of PM(10)in 16 urban, industrial and background sites in Italy, Atmosphere 11 (5) (2020) 22.

[22] A.A. Shaltout, M. Harfoushe, S.S.M. Ali, A.G. Karydas, P. Kregsamer, P. Wobrauschek, C. Streli, O.H. Abd-Elkader, M.A. Yassin, N.F. El Orabi, Elemental composition and source apportionment of atmospheric aerosols collected from urban and residential areas of Jordan using multi-secondary targets energy dispersive X-ray fluorescence, Spectroc. Acta Pt. B-Atom. Spectr. 170 (2020) 8.

[23] F. Lucarelli, M. Chiari, G. Calzolai, M. Giannoni, S. Nava, R. Udisti, M. Severi, X. Querol, F. Amato, C. Alves, K. Eleftheriadis, The role of PIXE in the AIRUSE project "testing and development of air quality mitigation measures in Southern Europe", Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms 363 (2015) 92–98.

[24] M. Ahmad, M.S. Rihawy, R. Haydr, M. Tlass, M. Roumie, A. Srour, PIXE and statistical analysis of fine airborne particulate matter (PM2.5) in Damascus, Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms 462 (2020) 75–81.

[25] S.M. Almeida, M.C. Freitas, C.A. Pio, Neutron activation analysis for identification of African mineral dust transport, J. Radioanal. Nucl. Chem. 276 (1) (2008) 161–165.

[26] M. Ogrizek, R. Jaćimović, M. Šala, A. Kroflič, No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters, Talanta 226 (2021), 122110.

[27] T. Szigeti, Z. Kertész, C. Dunster, F.J. Kelly, G. Záray, V.G. Mihucz, Exposure to PM2.5 in modern office buildings through elemental characterization and oxidative potential, Atmos. Environ. 94 (2014) 44–52.

[28] M. Žitnik, M. Jakomin, P. Pelicon, Z. Rupnik, J. Simčič, M. Budnar, N. Grlj, B. Marzi, Port of Koper - Elemental concentrations in aerosols by PIXE, Xray Spectrom. 34 (4) (2005) 330–334.

[29] W. Nischkauer, A. Izmer, M.A. Neouze, F. Vanhaecke, A. Limbeck, Combining dispersed particle extraction with dried-droplet laser ablation ICP-MS for determining platinum in airborne particulate matter, Appl. Spectrosc. 71 (7) (2017) 1613–1620.

[30] R.J.C. Brown, K.E. Jarvis, B.A. Disch, S.L. Goddard, An investigation of calibration materials for the measurement of metals in ambient particulate matter on filters by LA-ICP-MS, Int. J. Environ. Anal. Chem. 93 (3) (2013) 335–348.

[31] T.W. May, R.H. Wiedmeyer, A table of polyatomic interferences in ICP-MS, Atom. Spectrosc. 19 (5) (1998) 150–155.

[32] C.J. Chin, C.F. Wang, S.L. Jeng, Multi-element analysis of airborne particulate matter collected on PTFE-membrane filters by laser ablation inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 14 (4) (1999) 663–668.

[33] U.E.A. Fittschen, C. Streli, F. Meirer, M. Alfeld, Determination of phosphorus and other elements in atmospheric aerosols using synchrotron total-reflection X-ray fluorescence, Xray Spectrom. 42 (5) (2013) 368–373.

[34] P. Avino, G. Capannesi, A. Rosada, Source identification of inorganic airborne particle fraction (PM10) at ultratrace levels by means of INAA short irradiation, Environ. Sci. Pollut. Res. 21 (6) (2014) 4527–4538.

[35] H. Cho, K.B. Dasari, M.C. Lim, G.M. Sun, R. Jaćimović, Y.H. Yim, Application of k0-INAA method in preliminary characterization of KRISS urban airborne particulate matter certified reference material, Appl. Sci. 10 (19) (2020).

[36] X.X. Tang, Y. Qian, Y.C. Guo, N.N. Wei, Y.L. Li, J. Yao, G.H. Wang, J.F. Ma, W. Liu, Analysis of atmospheric pollutant metals by laser ablation inductively coupled plasma mass spectrometry with a radial line-scan dried-droplet approach, Spectroc. Acta Pt. B-Atom. Spectr. 138 (2017) 18–22.

[37] M.S. Robinson, I. Grgić, V.S. Šelih, M. Šala, M. Bitsui, J.T. Van Elteren, Laser ablation ICP-MS of size-segregated atmospheric particles collected with a MOUDI cascade impactor: a proof of concept, Atmos. Meas. Tech. 10 (5) (2017) 1823–1830.

[38] S. Tanaka, N. Yasushi, N. Sato, T. Fukasawa, S.J. Santosa, K. Yamanaka, T. Ootoshi, Rapid and simultaneous multi-element analysis of atmospheric particulate matter using inductively coupled plasma mass spectrometry with laser ablation sample introduction, J. Anal. At. Spectrom. 13 (2) (1998) 135–140.

[39] L. Samek, Z. Stegowski, L. Furman, Preliminary PM2.5 and PM10 fractions source apportionment complemented by statistical accuracy determination, Nukleonika 61 (1) (2016) 75–83.

[40] L. Samek, A. Gdowik, J. Ogarek, L. Furman, Elemental composition and rough source apportionment of fine particulate matter in air in Cracow, Poland, Environ. Prot. Eng. 42 (1) (2016) 71–83.

[41] X.C. Chen, J.J. Cao, T.J. Ward, L.W. Tian, Z. Ning, N.K. Gali, N.J. Aquilina, S.H. L. Yim, L.L. Qu, K.F. Ho, Characteristics and toxicological effects of commuter exposure to black carbon and metal components of fine particles (PM2.5) in Hong Kong, Sci. Total Environ. 742 (2020) 12.

[42] A.A. Shaltout, J. Boman, D.A.R. Al-Malawi, Z.F. Shehadeh, Elemental composition of PM2.5 particles sampled in industrial and residential areas of Taif, Saudi Arabia, Aerosol Air Qual. Res. 13 (4) (2013) 1356–1364.

[43] H. Jorquera, F. Barraza, Source apportionment of PM10 and PM2.5 in a desert region in northern Chile, Sci. Total Environ. 444 (2013) 327–335.

[44] T. Okuda, E. Fujimori, K. Hatoya, H. Takada, H. Kumata, F. Nakajima, S. Hatakeyama, M. Uchida, S. Tanaka, K.B. He, Y.L. Ma, H. Haraguchi, Rapid and simple determination of multi elements in aerosol samples collected on quartz Fiber filters by using EDXRF coupled with fundamental parameter quantification technique, Aerosol Air Qual. Res. 13 (6) (2013) 1864–1876.

[45] L. Qiao, R. Zhang, J. Qiao, X. He, Z. Wu, Preparation of ashless cellulose paper standards for rapid determination of multi-element concentrations in airborne fine particulate matter using laser ablation inductively coupled plasma mass spectrometry, RSC Adv. 11 (12) (2021) 6644–6653.

[46] F. Bilo, L. Borgese, A. Wambui, A. Assi, A. Zacco, S. Federici, D.M. Eichert, K. Tsuji, R.G. Lucchini, D. Placidi, E. Bontempi, L.E. Depero, Comparison of multiple X-ray fluorescence techniques for elemental analysis of particulate matter collected on air filters, J. Aerosol, Sci. 122 (2018) 1–10.

[47] A. Wagner, M. Mages, Total-Reflection X-ray fluorescence analysis of elements in size fractionated particulate matter sampled on polycarbonate filters - Composition and sources of aerosol particles in Goteborg, Sweden, Spectroc. Acta Pt. B-Atom. Spectr. 65 (6) (2010) 471–477.

[48] I. De La Calle, N. Cabaleiro, V. Romero, I. Lavilla, C. Bendicho, Sample pretreatment strategies for total reflection X-ray fluorescence analysis: a tutorial review, Spectroc. Acta Pt. B-Atom. Spectr. 90 (2013) 23–54.

[49] E. Bontempi, A. Zacco, D. Benedetti, L. Borgese, P. Colombi, H. Stosnach, G. Finzi, P. Apostoli, P. Buttini, L.E. Depero, Total reflection X-ray fluorescence (TXRF) for direct analysis of aerosol particle samples, Environ. Technol. 31 (5) (2010) 467–477.

[50] J. Prost, P. Wobrauschek, C. Streli, Quantitative total reflection X-ray fluorescence analysis of directly collected aerosol samples, Xray Spectrom. 46 (5) (2017) 454–460.

[51] R.J.C. Brown, K.E. Jarvis, B.A. Disch, S.L. Goddard, A.S. Brown, Spatial inhomogeneity of metals in particulate matter on ambient air filters determined by LA-ICP-MS and comparison with acid digestion ICP-MS, J. Environ. Monit. 11 (11) (2009) 2022–2029.

[52] Y.K. Hsieh, L.K. Chen, H.F. Hsieh, C.H. Huang, C.F. Wang, Elemental analysis of airborne particulate matter using an electrical low-pressure impactor and laser

ablation/inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 26 (7) (2011) 1502–1508.
[53] M. Almeida-Silva, S.M. Almeida, J. Cardoso, T. Nunes, M.A. Reis, P.C. Chaves, C. A. Pio, Characterization of the aeolian aerosol from Cape Verde by k(0) INAA and PIXE, J. Radioanal. Nucl. Chem. 300 (2) (2014) 629–635.
[54] S.M. Almeida, M.C. Freitas, M. Reis, T. Pinheiro, P.M. Felix, C.A. Pio, Fifteen years of nuclear techniques application to suspended particulate matter studies, J. Radioanal. Nucl. Chem. 297 (3) (2013) 347–356.
[55] X.N. Lei, R.J. Chen, C.C. Wang, J.J. Shi, Z.H. Zhao, W.H. Li, J. Bachwenkizi, W. Z. Ge, L. Sun, S.Q. Li, J. Cai, H.D. Kan, Necessity of personal sampling for exposure assessment on specific constituents of PM2.5: Results of a panel study in Shanghai, China, Environ. Int. 141 (2020) 9.
[56] S.M. Almeida, M.A. Reis, M.C. Freitas, C.A. Pio, Quality assurance in elemental analysis of airborne particles, Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms 207 (4) (2003) 434–446.
[57] T. Dourado, H. Gemeiner, A.C.F. Gomes, E. Almeida, A.C. da Silva, N. Valadao, A. A. Menegario, J.S. Govone, D. Gastmans, Elemental composition of particulate matter in the southeastern brazilian ceramic pole by synchrotron radiation X-ray fluorescence technique (SR-XRF), J. Braz. Chem. Soc. 31 (6) (2020) 1203–1215.
[58] E.E. Agency, Air Quality in Europe - 2019 Report, 2019.
[59] R.J.C. Brown, K.E. Jarvis, B.A. Disch, S.L. Goddard, E. Adriaenssens, N. Claeys, Comparison of ED-XRF and LA-ICP-MS with the European reference method of acid digestion-ICP-MS for the measurement of metals in ambient particulate matter, Accredit. Qual. Assur. 15 (9) (2010) 493–502.

## 3.2 Article 2: No More Waste at the Elemental Analysis of Airborne Particulate Matter on Quartz Fibre Filters

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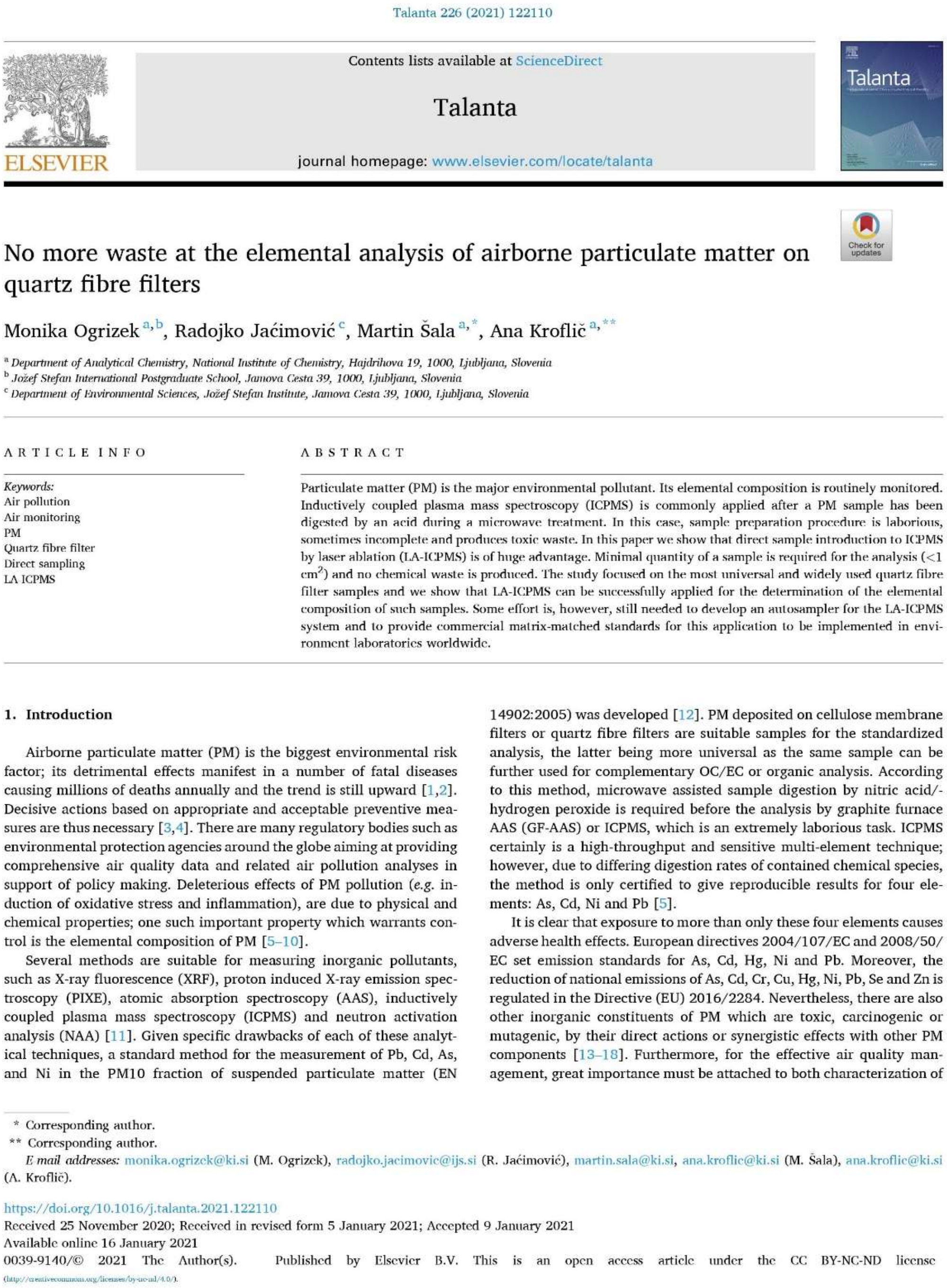
Trace elements are one of the PM constituents responsible for its chemical toxicity and other adverse effects. That is also why in EU, concentrations of As, Cd, Ni, and Pb are regularly monitored in airborne PM by national agencies (EU directives 2004/107/EC and 2008/50/EC). The current standard method prescribed for this purpose requires a sample pre-treatment step by MW using concentrated nitric acid and hydrogen peroxide to transform the sample in the liquid form, which is compatible with the ICPMS or GFAAS instrument for the analysis. Especially the MW pre-step, however, can be a source of many errors and is incriminating to the environment. Among the most important aspects are: i) the prescribed protocol does not assure efficient digestion of any PM matrix, which can consequently hinder accurate determination of some elements (others than the listed four), and ii) since the analysis is performed in such a large scale (diurnal monitoring at many sampling sites all around the world), huge amounts of toxic chemicals are used on a daily basis, which eventually end up as toxic waste and burden the environment. In this article we present a new method for the determination of elemental concentration in ambient air directly from the most convenient quartz fiber filters loaded with PM.

The LA-ICPMS method was developed for direct, multi-element determination of PM without any pre-treatment and with minor burden for the environment. In the paper, a comprehensive procedure is described, from method development to the required data processing, including additional partial method validation with the assessment of accuracy and LOD. The samples used for the method development were donated by ARSO, providing us also with the corresponding elemental concentrations determined in advance by the standard MW/ICPMS method as part of their air-quality monitoring routine. The method development consisted of the optimization of LA (*i.e.* laser beam size, scan speed, fluence, dosage, ablation pattern, washout time) and ICPMS instrumental parameters (*i.e.* acquisition and dwell times), assessment of background and filter blank, determination of sampling procedure, data processing and quantification.

Special attention was paid to the sampling procedure, which is strongly dependent on the homogeneity of PM deposited on a filter. Possible radial dependence of sampling, individual spikes and their post-processing, and the sub-sample size needed for the analysis to be still representative of the whole sample were carefully examined. The sub-sample size was statistically evaluated at a 95 % confidence interval. Another challenge was calibration, because LA-ICPMS requires a matrix-matched standard material, which is not commercially available for the elemental composition of PM deposited on quartz fiber filters specifically.

One idea was to use commercial RM of PM on quartz fiber filter (NIST RM 8785), which is not certified for elemental composition, however, NIST 8785 was produced by deposition of dust RM NIST 1649a on a quartz-fiber filter, and NIST 1649a does have a certified elemental composition. However, it turns out this RM was not matrix-matched for the tested samples and was not suitable for quantification. Therefore, different approach had to be applied. Some of the urban samples with known elemental composition by the standard MW/ICPMS were additionally quantified with absolute method $k_0$-INAA and used as a standard material for the quantification of LA-ICPMS measurements. The proposed approach is a possible solution in research, however, for routine monitoring, a commercially available alternative will have to be provided. At the end, 11 ambient PM samples were analyzed with the developed LA-ICPMS and the standardized MW/ICPMS methods, among which 3 were also measured with $k_0$-INAA. Comparison between the methods was statistically assessed with a non-parametric bootstrap paired t-test.

The presented LA-ICPMS method circumventing the MW pre-step turned out to be green, fast, accurate with a low LOD, requires a minimal amount of sample, and is capable of the determination of at least 20 elements at a time (*e.g.* Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, V, and Zn). As such, it certainly is a valid alternative to the standard MW/ICPMS method, however some more development in the direction of certified standard materials and automatization is still required before it can be proposed and validated as a standard method.



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# No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters

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ABSTRACT

Particulate matter (PM) is the major environmental pollutant. Its elemental composition is routinely monitored. Inductively coupled plasma mass spectroscopy (ICPMS) is commonly applied after a PM sample has been digested by an acid during a microwave treatment. In this case, sample preparation procedure is laborious, sometimes incomplete and produces toxic waste. In this paper we show that direct sample introduction to ICPMS by laser ablation (LA-ICPMS) is of huge advantage. Minimal quantity of a sample is required for the analysis ($<1$ cm$^2$) and no chemical waste is produced. The study focused on the most universal and widely used quartz fibre filter samples and we show that LA-ICPMS can be successfully applied for the determination of the elemental composition of such samples. Some effort is, however, still needed to develop an autosampler for the LA-ICPMS system and to provide commercial matrix-matched standards for this application to be implemented in environment laboratories worldwide.

## 1. Introduction

Airborne particulate matter (PM) is the biggest environmental risk factor; its detrimental effects manifest in a number of fatal diseases causing millions of deaths annually and the trend is still upward [1,2]. Decisive actions based on appropriate and acceptable preventive measures are thus necessary [3,4]. There are many regulatory bodies such as environmental protection agencies around the globe aiming at providing comprehensive air quality data and related air pollution analyses in support of policy making. Deleterious effects of PM pollution (*e.g.* induction of oxidative stress and inflammation), are due to physical and chemical properties; one such important property which warrants control is the elemental composition of PM [5–10].

Several methods are suitable for measuring inorganic pollutants, such as X-ray fluorescence (XRF), proton induced X-ray emission spectroscopy (PIXE), atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICPMS) and neutron activation analysis (NAA) [11]. Given specific drawbacks of each of these analytical techniques, a standard method for the measurement of Pb, Cd, As, and Ni in the PM10 fraction of suspended particulate matter (EN 14902:2005) was developed [12]. PM deposited on cellulose membrane filters or quartz fibre filters are suitable samples for the standardized analysis, the latter being more universal as the same sample can be further used for complementary OC/EC or organic analysis. According to this method, microwave assisted sample digestion by nitric acid/-hydrogen peroxide is required before the analysis by graphite furnace AAS (GF-AAS) or ICPMS, which is an extremely laborious task. ICPMS certainly is a high-throughput and sensitive multi-element technique; however, due to differing digestion rates of contained chemical species, the method is only certified to give reproducible results for four elements: As, Cd, Ni and Pb [5].

It is clear that exposure to more than only these four elements causes adverse health effects. European directives 2004/107/EC and 2008/50/EC set emission standards for As, Cd, Hg, Ni and Pb. Moreover, the reduction of national emissions of As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn is regulated in the Directive (EU) 2016/2284. Nevertheless, there are also other inorganic constituents of PM which are toxic, carcinogenic or mutagenic, by their direct actions or synergistic effects with other PM components [13–18]. Furthermore, for the effective air quality management, great importance must be attached to both characterization of

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suspended PM and the identification of its sources, elemental composition being very supportive of the latter. More and accurately determined elements could improve source apportionment, especially the performance of receptor models [19]. Therefore, a new method for its determination would be of huge advantage, providing reliable and reproducible concentrations of a series of elements contained in ambient PM, preferably suitable for quartz fibre filters samples. Ideally, the improved method would allow for fast trace analysis with no additional burden to the environment.

To date, there have been applications of laser ablation (LA) as a direct introduction system of solid PM to ICPMS (LA-ICPMS), avoiding the restrictive and time-consuming sample preparation step in the conventional method [20–29]. However, to the best of our knowledge, only two studies exist on the application of LA-ICPMS to quartz fibre filter samples. The first dates back in 1994 [30] and despite the series of successful research on other filter types in the following two decades, the next one using quartz fibre filters is only the very recent study of Tang et al. [31]. In outline of the cited literature, LA-ICPMS is suitable for the multi-element analysis of atmospheric PM samples. It is recognized faster than the conventional method by acid digestion, its direct sampling reduces the risk of contamination and improves laboratory safety. LA-ICPMS allows for ultratrace elemental analysis with the repeatabilities of most elements within 15%. The main problems common to all these studies are questions of sample homogeneity and calibration, which still need to be resolved.

In this work we developed a protocol for the determination of levels of elemental pollution in ambient air using LA-ICPMS on quartz fibre filter samples. Compared to the conventional method by microwave digestion and ICPMS (MW-ICPMS), we demonstrate its supreme performance in terms of high-throughput, multi-element capabilities, improved sensitivity and environmental sustainability, and advocate its use in air quality control laboratories. Moreover, we identify necessary steps to support the utilization of this green analytical technique in routine analyses, replacing the conventional method that requires laborious acid digestion and eliminating toxic waste.

## 2. Materials and methods

### 2.1. Samples and standard materials

Samples of ambient PM10 on quartz fibre filter (PALL, USA; filter diameter 150 mm) were donated by the Slovenian Environment Agency (ARSO). For sampling, a high volume sampler (Digitel DHA-80 Aerosol Sampler, Switzerland) was used. Samples were being collected for 24 h at the flow rate of 500 l min$^{-1}$ (approx. 720 m$^3$ air was sampled through each filter). To study differently loaded samples, they were collected in several towns around Slovenia (Maribor, Murska Sobota, Zagorje, Kranj, and Žerjav) and in different seasons (details are listed in Table S1). The samples from Maribor (111,000 inhabitants) are representative of an urban environment with residential and commercial characteristics. The sampling site of Kranj (56,000 inhabitants) is classified as an urban background and Murska Sobota (19,000 inhabitants) is classified as suburban background with rural characteristics. Zagorje (17,000 inhabitants) and Žerjav (370 inhabitants) are towns with strong industry and the main pollution emissions come from industry, traffic, and individual combustion sources.

Parameters optimization was performed on four samples from Maribor with different PM mass loadings: two low-loaded samples from July 2015 and two high-loaded samples from December 2015 were used. Other samples were used for the homogeneity testing and the comparison with standard and reference methods (see details in Table S1). Additionally, unused quartz fibre filters (PALL, USA) were used as filter blanks.

NIST RM 8785 (PM deposited on quartz filter) was tested as a possible standard material for quantification purposes. NIST SRM 612 was used to monitor the instrument drift during long-time LA-ICPMS measurements. Certified reference material BCR-320R Channel sediment was used for $k_0$-INAA QA/QC purposes.

### 2.2. Analytical methods

#### 2.2.1. Standard method (MW-ICPMS)

According to EN 14902:2005, As, Cd, Ni and Pb can be determined in PM10 from ambient air by microwave assisted acid digestion and ICPMS. This analysis has been performed by ARSO as a part of their air quality monitoring. Only briefly, a subsample of a filter sample (3 × Ø30 mm, which accounts for approx. 21 cm$^2$) was digested with $HNO_3$ (8 ml) and $H_2O_2$ (2 ml) according to the predefined temperature program, retaining maximum digestion temperature 220 °C for 25 min. After cooling, the digest was diluted to 100 ml with miliQ water and analysed by ICPMS.

Altogether, 22 elements (Ag, Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, Ga, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Tl, V, Zn) were analysed according to this method, although the standard method is only verified for the 4 specified elements (As, Cd, Ni and Pb). The results were not corrected for filter blanks, because they were all bellow LOD.

#### 2.2.2. LA-ICPMS

LA is a way of sample sampling that does not require any sample pretreatment. It uses the energy of a laser beam to remove the material from a solid surface. As the applied laser beams are very narrow (down to 1 μm), this microanalytical technique allows for spatially resolved analysis. Filter samples were mounted to glass microscope slides with a double-sided tape (Scotch, USA) and directly analysed for their elemental composition. Measurements were performed by a nanosecond excimer laser ablation system (193 nm ArF*; Analyte G2, Teledyne Photon Machines Inc., Bozeman, MT) interfaced with a quadrupole ICPMS instrument (Agilent 7900x, Agilent Technologies, Santa Clara, CA). Ablation took place in a HelEx II two-volume ablation cell. The ablated material was transported to ICPMS with helium as a carrier gas (cup flow = 0.5 l min$^{-1}$; cell flow = 0.3 l min$^{-1}$) and with the addition of argon as a makeup gas (0.8 l min$^{-1}$).

The following 23 elements were tested for their suitability for laser ablation: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, V, and Zn. If the signal of a sample did not differ significantly from the signal of gas blank (as in the case of Se), this specific element was further investigated by measuring only one element at a time, i.e. with a longer dwell time equal to the acquisition time. Method parameters were optimized for the 4 elements specified in the standard method (As, Cd, Ni and Pb), while sample homogeneity was assessed by measuring 10 elements at a time (As, Cd, Cr, Cu, K, Mn, Ni, Pb, V, and Zn). For quantification, 20 representative elements were finally elected for simultaneous analysis (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Tl, V, and Zn).

Only in the case of the homogeneity testing, instrumental analysis lasted for about 9 h; therefore, a possible drift of the instrument with time was also assessed during this measurement. NIST SRM 612 glass was ablated at the beginning and approx. every 30 min until the end of the experiment. The data were corrected for the recorded drift in the NIST standard before further analysis.

#### 2.2.3. Reference method ($k_0$-INAA)

An aliquot of an air-dry sample (approx. 5.0 cm$^2$; 0.034–0.045 g) was sealed in a polyethylene ampoule (SPRONK System, The Netherlands). To determine short-lived radionuclides, the aliquot of a sample was irradiated with the standard Al-0.1% Au alloy (IRMM-530R) for 5 min, and for the determination of long-lived radionuclides, the same aliquot was irradiated for 12 h after the appropriate cooling time (>14 days). Irradiation was performed in the carousel facility of the 250 kW TRIGA Mark II nuclear reactor of the Jožef Stefan Institute, Ljubljana. After short irradiation (5 min), gamma activity of induced radionuclides in a sample was measured after 5 and 35 min of cooling; after long irradiation (12 h), it was measured after 3, 7–10 and 22 days of cooling. All measurements were performed on an absolutely calibrated HPGe detector (45% relative efficiency). HyperLab 2002 [32] was used to evaluate gamma spectra and the element content was calculated using Kayzero for Windows software [33]. As $k_0$-INAA measures element concentrations in the whole filter (filter matrix and PM deposit), a blank filter was separately analysed and each measurement value was corrected for the blank.

As a result, 7 elements (As, Fe, K, Mn, Sb, V, and Zn) were successfully determined by $k_0$-INAA in the studied samples. The other detected elements were either below LOD after the blank subtraction or could not be determined due to impurities in a filter blank.

### 2.3. Data analysis

#### 2.3.1. Homogeneity assessment – radial dependence

Ten ablation lines were ablated along the radius (from the edge to the centre each time) of 7 differently loaded filters (see Table S1) and the image was plotted in ImageJ where the data was assessed for trends (ascending or descending signal and edge effect).

#### 2.3.2. Homogeneity assessment – spikes

A sufficiently large surface area of a filter (approx. 8.6 cm$^2$ corresponding to 5% of the whole filter) was ablated and the obtained data images (pixel matrices) were taken for statistical analysis. All matrices were inspected for intensity variability in ImageJ. Many spikes were observed and some were considered outliers (refer here to the explanation in the Results section). The threshold set for outliers was based on three interquartile ranges (IQR), which is calculated as the range between the third ($Q_3$) and the first quartile ($Q_1$) of the data as in equation (1). Low (2) and high (3) threshold limits for outliers were set at three IQR subtracted from $Q_1$ or added to $Q_3$, respectively. All data points out of this range were removed before further analysis.

$$IQR = Q_3 - Q_1 \tag{1}$$

$$low = Q_1 - 3(IQR) \tag{2}$$

$$high = Q_3 + 3(IQR) \tag{3}$$

#### 2.3.3. Homogeneity assessment – representative sample size

The same data matrices were further analysed in program R [34] with a script specially written for this purpose. The script contains formulas provided in the raster package in R [35]. Prior to statistical analysis, the matrices were corrected for the instrument drift and outliers were eliminated (vide supra).

The applied statistical approach is schematically presented in Fig. 1. Since the objective of this analysis was to find the smallest sample area still representative of the whole ablated filter surface, the ablated area was considered to be a statistical population of pixels and the average of all pixels in the matrix was taken as its true value (total average). In the next step, the matrix was divided into equal non-overlapping units (rectangles sizes m × n pixels), which were created to satisfy the condition of random sampling given the method used. Note that it is easier and more useful to ablate small units with dimensions m × n pixels than individual pixels randomly scattered throughout the whole filter area. The average of pixels in each unit was calculated and taken as the average value of a unit ($\bar{x}$). Further, subsamples consisting of N = 3 randomly selected units were statistically assessed. The average and confidence interval of each subsample were calculated and compared with the total average, to evaluate if the subsample is representative of the whole population. By analysing all possible subsamples in the population (all combinations of three units were considered) the percentage of representative subsamples was estimated for each unit size.

In theory, if sampling is statistically sound and confidence level (1-α) is set to 95%, then 95% of all subsamples contain the true value of the population within their confidence interval, which is dependent on the number of units in a subsample (N) and the standard deviation between

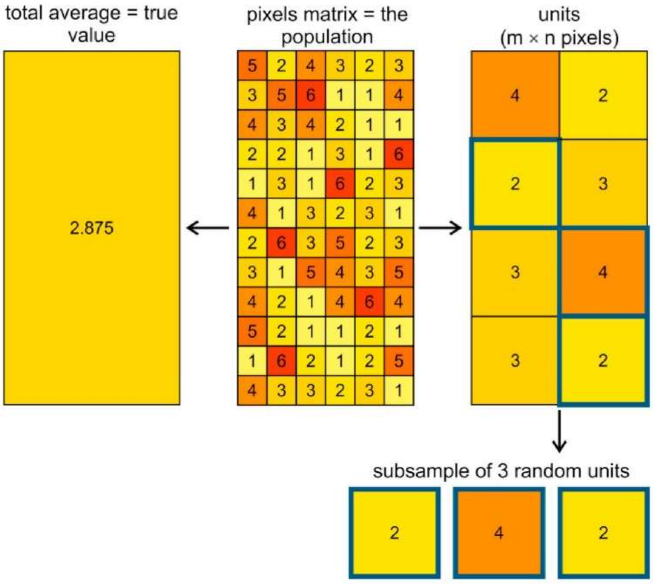

**Fig. 1.** Schematic representation of how the smallest representative subsample size was determined. Pixel matrix (middle) was considered to be a population; the numbers represent counts obtained by LA-ICPMS. The average of all pixels was taken as the total average or true value of the population (left). Pixel matrix was divided into equal size units (right) consisting of m × n pixels (in the above example 3 × 3 pixels). The average of all pixels within the unit was taken as a value of the unit, which was used to calculate an average and a confidence interval of a subsample. A subsample was a combination of three random units, which was repeated for all possible combinations.

these units (sd). The limits of confidence interval ($l_{1,2}$) can be calculated by equation (4). $t_{\alpha/2}$ was taken from the standardized values based on the student statistics and is defined by the significance level ($\alpha = 0.05$) and the degrees of freedom (N-1).

$$l_{1,2} = \overline{x} \pm t_{\alpha/2}\frac{sd}{\sqrt{N}} \tag{4}$$

The analysis consisted of several runs and in each run, the matrix was divided into smaller units. The condition for the subsample to be considered representative of the whole population was: (i) its 95% confidence interval contains the total average of the population, and (ii) the size of its confidence interval does not exceed 0.3-times the subsample average. The latter is a safety step to exclude extremely wide confidence intervals, which could result in subsample averages very distant from the total average of the population. Finally, the size of units in a subsample was considered adequate (*i.e.*, representative of the whole population) if 95% of all possible subsamples in a run contained the total average within their confidence interval, given that the confidence interval did not exceed 0.3 × subsample average.

### *2.3.4. Method comparison*

A comparison between three different methods (MW-ICPMS, LA-ICPMS and $k_0$-INAA) was made in program R [34] with the raster [35], rgdal [36] and reshape2 [37] packages for data manipulation, the car [38] package for assessing the equality of variances, and the ggplot2 [39] and ggtern [40] packages for graphical presentation of the data. For this purpose, three differently loaded samples were analysed by $k_0$-INAA and eleven samples from different sites and seasons were analysed by LA-ICPMS and MW-ICPMS. A nonparametric bootstrap paired *t*-test (NPBPT) was used for statistical analysis. Based on the study of Dwivedi et al. [41]. on the reliability of statistical testing in the case of small sample sizes, we assume good statistical power for any comparison made with NPBPT and n = 3 sample size in the case of equal variances (15% chance for type II error), whereas n = 3 sample size analyses with unequal variances should be taken with caution (49% chance for type II error). Moreover, any comparison with the sample size of n = 11 can be attributed high statistical power (very low chance for type II error) when variances are either equal or unequal. For details on this see the Supplementary Information file, section 6. Statistical Information.

Three paired comparisons (MW-ICPMS vs. LA-ICPMS, MW-ICPMS vs. $k_0$-INAA, and LA-ICPMS vs. $k_0$-INAA) were made with use of NPBPT applying the R code reported recently [41]. Every pair was tested for comparison of 6 elements (As, Fe, Mn, Sb, V, Zn), plus K concentration was compared between LA-ICPMS and $k_0$-INAA (unfortunately, K was not determined by MW-ICPMS). For each paired comparison, the assumption of variances equality was also tested with the Levene's test. The significance level α was chosen to be 0.05 for all tests. If the resulted p-value from statistical tests was lower than α, the paired comparison observed a statistically significant difference between the methods (NPBPT) or unequal variances (Levene's test).

## 3. Results

### *3.1. Instrument parameters optimization*

LA-ICPMS is a technique sensitive to the nature of sample material and therefore needs thorough optimization to assure the best possible sensitivity and repeatability. Luckily, a wide parameter space is available to tune for the needs of a specific sample type. Some of the parameters can be chosen by experience/development in the field from the last years when the technique has made a significant progress driven by the development of fast aerosol transport technologies [42] and strategies for best image quality [43,44]. For this, knowing sample characteristics is paramount, in our case PM material deposited on a quartz fibre filter.

PM is a mixture of heterogeneous particles (PM10 are airborne particles of diameter less than 10 μm) which are, after air sampling, mostly loaded on the top of a quartz fibre filter and caught in the upper layers of the filter fibres. Hence, with the optimization of instrument parameters (Fig. 2), one can assure suitable fractional ablation, *i.e.* the ablation of total deposited PM and minimal amounts of quartz fibres minimizing the noise arising due to the filter blank, which substantially improves measurement sensitivity. Yet, the method must be robust enough not to be influenced by filter loading (*i.e.*, the amount of PM deposited on the filter). According to EEA 2019 air quality report, average daily PM10 concentrations normally range below 75 μg $m^{-3}$ in the majority of European cities [45]. We used typical 24 h high-volume PM10 samples of air concentrations up to 97 μg $m^{-3}$ in this study, 30 μg $m^{-3}$ being the threshold between low- (bellow) and high-loaded filters (above). For more details about the samples used see the Supplementary Information file, Table S1 and Fig. S1.

Despite of the fractional ablation, impurities in a filter matrix which mostly consists of $SiO_2$ can contribute to the measured signal resulting in a positive bias of the measurement. Therefore, a blank filter was ablated and the signals for most of the measured elements (except for Se, data not shown) did not differ significantly from the signals for gas blank, *i.e.*, the background signals of the measurement (Fig. S2). Note that this approach considers the worst case scenario, because in the absence of any PM material more filter fibres were ablated as would be in the case

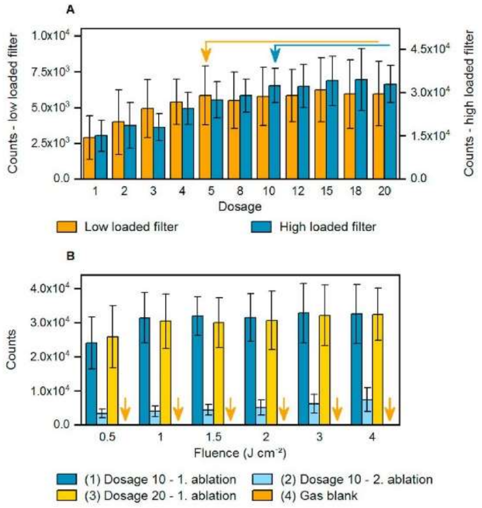

**Fig. 2.** Laser ablation performance optimization – an example for Pb. (A) represents increasing dosage vs. signal intensity on low and high loaded filters. The signal is rising with the increasing dosage until a plateau is reached, where all of the deposit is removed by ablation (above dosage 5 and 10 for low and high loaded filters, respectively). (B) represents increasing fluence vs. signal intensity on a high loaded filter with dosage 10 and 20. in the case of dosage 10, the same filter area was subjected to another ablation pass. The signal reaches a plateau above 1 J $cm^{-2}$ and there is no significant difference between dosage 10 and 20, which indicates that all of the deposited material is removed with dosage 10 already. The signal for gas blank is also plotted, always being more than 100-times lower than the other signals. The curious result from the second pass (the signal is expected to be zero if all the material has been ablated in the first pass) probably results from ejecta (the remaining material from nearby ablation that was not transferred to ICPMS) and cannot be avoided. The ejecta is increasing with fluence because harsher ablation conditions produce more ejecta.

of PM-loaded filter samples. Therefore, no measurement corrections need to be applied in this regard.

The sensitivity was further fine-tuned for each of the elements analysed. Individual dwell times were ascribed to each element of interest depending on its relative abundance in the samples and the number of elements analysed simultaneously (Table S2). We used long dwell times for rare elements, whereas abundant elements were always analysed with shorter dwell times. With doing this, the time saved for the analysis of less ubiquitous elements assured their sufficiently low limits of detection (LOD). Every time, the sum of all dwell times roughly corresponded to the overall acquisition time set for the measurement, which could theoretically be also prolonged if very rare elements were sought in a sample (resulting in improved sensitivity but longer analysis time). The estimated LOD (Table 1) go down to $10^{-3}$ ng $m^{-3}$ and are flexible (vide supra).

Parameters summarized in Table 2 were optimized for the four standardized elements (As, Cd, Ni and Pb) using daily high-volume PM10 samples of air mass concentrations up to about 70 μg $m^{-3}$, which is typical for Europe. More details about the selection of fixed parameters is given in Supplementary Information. In all of the following experiments, these optimized instrument parameters were used. Moreover, in Table S2 are gathered dwell times used, depending on the number of elements analysed simultaneously.

### 3.2. Homogeneity and sub-sampling

The optimization described in the above section gave us optimal instrument parameters needed for the best sensitivity of the developed method in a reasonable analysis time. On the other hand, reproducibility of filter analysis by LA-ICPMS must also be assured. Sub-sampling of a filter sample for laser ablation is crucial in this step and is elaborated hereafter.

It is generally accepted that PM is homogeneously distributed over the filter area. This is, however, a rather vague statement as homogeneity is a relative measure and depends on a scale on which the object is observed. For example, with the naked eye soil is observed homogeneous. But if it is looked under the microscope, different particles, microorganisms or even molecules can be distinguished. Homogeneity can, therefore, be differently interpreted depending on the experimental question.

In EN 14902:2005, sub-sampling is allowed, but not exactly prescribed. On the other hand, EPA prescribes consumption of 1/9 of a high-volume filter sample, corresponding to roughly 20 $cm^2$ [11]. We took advantage of LA-ICPMS and investigated some PM samples with a great resolution. The minimal area that can be technically ablated with LA goes down to about a $\mu m^2$ (the size of a laser beam), which allows to study the composition of a sample on a μm scale. We started with the biggest possible laser beam (128 μm) and already at this scale filter sample could no longer be considered homogeneous, which is due to variations in particle sizes, their composition, and the unequal intertwining of filter fibres. One such example is shown in Fig. S3, which puts the homogeneity of PM material on a filter under question and complicates any analysis in which filter sample is not completely consumed. Similar has already been observed by XRF [46], LA-ICPMS [47] and GF-AAS [48].

**Table 1**
Estimated limits of detection (LOD in ng element per $m^3$ air) for the three methods compared: MW-ICPMS, LA-ICPMS and $k_0$-INAA.

| | | | | EPA | |
|---|---|---|---|---|---|
| | MW-ICPMS[a] (ng $m^{-3}$) | $k_0$-INAA[b] (ng $m^{-3}$) | LA-ICPMS[c] (ng $m^{-3}$) | MW-ICPMS[d] (ng $m^{-3}$) | NAA[d] (ng $m^{-3}$) |
| As | 0.14 | 0.10 | 0.06 | 0.30 | 0.09 |
| Fe | 15.28 | 39.54 | 2.3 | – | 4629.0 |
| K | – | 70.86 | 1.739 | – | 0.92 |
| Mn | 0.42 | 0.05 | 0.084 | 0.02 | 0.02 |
| Sb | 0.21 | 0.02 | 0.17 | 0.01 | 0.4 |
| V | 0.03 | 0.21 | 0.01 | 0.01 | 0.04 |
| Zn | 6.94 | 1.43 | 0.49 | 0.04 | 9.2 |

All LOD refer to PM samples collected with a high-volume air sampler for 24 h.

[a] A this is a method detection limit based on 1/8 of a filter sample used in the pretreatment step;

[b] LOD was calculated according to $LOD = 2.706 + 4.653\sqrt{B}$, B being the background calculated for the energy interval where the full-energy peak is expected in the gamma spectrum [33];

[c] the reported LOD refer to instrument parameters and were conservatively estimated as 5-times standard deviation of gas blank, they are optimized for the least abundant elements and flexible within the set acquisition time (and beyond);

[d] method detection limits as reported in EPA's Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air [11].

**Table 2**
Optimal instrument parameters for the ablation of PM on quartz fibre filter with LA-ICPMS.

| Pre determined parameters by educated guess: | |
|---|---|
| Laser beam size | 128 μm (square mask) |
| Scan speed | 256 μm $s^{-1}$ |
| Acquisition time | 0.5 s |
| **Optimized parameters:** | |
| Repetition rate | 20 Hz |
| Fluence | 1.5 J $cm^{-2}$ (with 10× demagnification) |
| Ablated area | 3 × 12 $mm^2$ (random sampling) |

24 h high-volume PM10 samples of air mass concentrations up to about 70 μg $m^{-3}$ were used.

The literature reports on radial dependences of element concentrations in investigated samples [31,46,47]. The uniformity of PM mass loading was thus first examined as a function of a distance from the filter centre. Recently, the radial effect has been attributed to the deviation in the ablation of irregular quartz fibre filter material [31], whereas the other study observed no statistical differences as a function of the position along the filter radius [48]. Indeed, we did not observe any trend in the output signal in the radial direction; an example is shown in Fig. 3 (note observed spikes are discussed below). This allowed us to conclude that PM material is uniformly distributed over the filter sample if only the filter material used and the sampler are of good quality and operation.

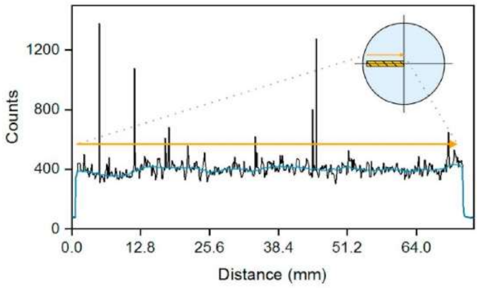

**Fig. 3.** Mass loading homogeneity assessment in the radial direction – an example for As. Average signal intensity for As is presented for 10 adjacent laser lines (length 60 mm) from the edge to the centre of KR 23. 01. 2018 filter sample. Top right side denotes the actual position of ablation lines on the filter. It can be seen that there is no evident trend that would exhibit non-uniform mass loading deposition. Sharp peaks (spikes) can also be observed, which were found randomly distributed over the filter area and confirmed as real nanoparticles in another experiment presented in Supplementary Information Fig. S4.

The smaller the subsample size, the faster the analysis; therefore, in the next step homogeneity was assessed in a sense of finding the smallest filter area that is representative of the whole filter sample. In other words, we were interested in how small parts of a sample still give us statistically the same characteristics as for the whole. A relatively large surface area corresponding to 5% of the whole filter was ablated for this purpose with 10 elements being measured simultaneously (see the Methods section for the list of elements). The result was a matrix of 58,000 data points (pixels) per element, which can be considered a 2D image of the elemental distribution on a filter or an element map (Fig. S3a). Due to long-time measurements (about 9 h), a possible drift of the instrument with time was also taken into account; refer here to the Methods section for details.

Large signal deviations in a positive direction (spikes in the range from 1 to a few pixels; see Fig. S3) were observed randomly distributed over the filter area. Another experiment was thus performed to confirm that these are real particles and not just a measurement artefact. Nanoparticle (NP) analysis has recently been made possible by LA-ICPMS if the number concentration of NP in a sample is low enough, which is true in our case (roughly 1%) [49]. As a rule, every measured peak that lasts approximately 500 µs can be considered a NP [50]. Two real samples were analysed with the total acquisition time set to 100 µs while only one element being measured at a time. Numerous 500 µs peaks were observed in both analysed samples (see Fig. S4 for an experimental example).

The abundance of spikes belonging to real particles with significantly different composition from the rest of deposited PM material was normally less than 1% of all data points. These, however, cause inhomogeneity of a filter sample, which manifests in an overall large signal standard deviation. Due to these irregularities, the average of a group of pixels is often excessively larger than its median (see Fig. S3), which is not in favour of our method optimization towards the smallest sample size required for the analysis. Nevertheless, if all those spikes were from specific particles of the same composition (which is never the case) and all in 10-time excess concentration compared to the average PM particle on the filter, 1% of such particles would add up 9% mass to the whole PM sample. Taking this as an upper limit of possible error made by their elimination, 9% is still below the repeatability and reproducibility of the standard method by MW-ICPMS. Therefore, appearing spikes were not recognized as carriers of the main information we are looking for, which is the average property of collected PM, so we consider them outliers in our protocol for data analysis. For the rule by which spikes are categorized as outliers, see the Methods section. It will be shown later on that the elimination of spikes prior to further analysis allows for much smaller sub-sampling for accurate analysis within the acceptable measurement error, which simultaneously shortens the time of analysis and reduces consumption of noble gases needed for the analysis. Nevertheless, we believe that the number and the composition of specific nanoparticles detected provide additional information on the origin and characteristics of collected PM, which can be interpreted in favour of source apportionment especially. This, however, is out of scope of this work.

After the drift correction and the elimination of outliers, the matrix was taken for statistical analysis. In reality, the data for the whole population is almost never available; in support of our experimental question, however, we assumed that the ablated matrix represented the whole population. The large filter area ablated was thus considered a statistical population where 95% subsamples should contain the average of the population within their confidence interval (1 − α = 95%). Furthermore, in order to calculate the confidence interval, which was needed to make a comparison, at least three repetitions were required. The pixel matrix was thus divided into non-overlapping units, whereas each sub-sample taken for comparison with the population consisted of 3 randomly selected units. By doing this, we were able to compare all possible subsamples with the whole population. Hence, the applied approach provided a subsample size at which 95% of all possible subsamples were representative of the whole ablated area. Conversely, there was no more than 5% of nonrepresentative subsamples of this size in the population.

The applied statistical analysis consisted of several runs with decreasing unit sizes and as a result, we report on the smallest subsample size that has the same characteristics as the whole population with 95% confidence. As demonstrated in Fig. 4, with decreasing the size of units (at the same time the size of individual subsamples also decreases), the percentage of representative subsamples which contain the population average within their 95% confidence interval also decreases. When analysing 3 unit-subsamples, the smallest area representative of the whole matrix was 3 × 12 mm$^2$ for most of the tested elements (As, Cr, Cu, K, Mn, Ni, Pb, Zn). The exceptions were Cd and V, which resulted in somehow bigger unit sizes: 3 × 23.8 mm$^2$ and 3 × 95 mm$^2$, respectively. This study provided sufficiently small unit sizes to perform LA-ICPMS measurements within a reasonable analysis time (less than 30 min per sample).

### 3.3. Quantification

For accurate quantification in LA-ICPMS, a matrix matched standard is required; hence the ablation rate of both materials is identical. Currently, there is no commercially available standard for airborne particulates deposited on quartz fibre filter with certified element concentrations. NIST RM 8785 is PM deposited on quartz fibre filter, but is primarily intended for carbon speciation and is thus not certified for its elemental composition. However, NIST RM 8785 is produced by capturing the fine fraction of NIST SRM 1649a (urban dust) on a quartz filter, which indeed has certified concentrations of some elements. Therefore, we intended to estimate element concentrations on NIST RM 8785 with use of mass depositions and the available certified concentrations for NIST SRM 1649a urban dust.

Three differently loaded NIST RM 8785 standards were analysed according to the developed protocol, 20 elements being measured simultaneously (for details refer to Table S1 and the Methods section). Unfortunately, we were not able to construct useful calibration curves. In most cases, the signal intensity from LA-ICPMS did not coincide with the increasing mass loading of NIST standards. Even with visual

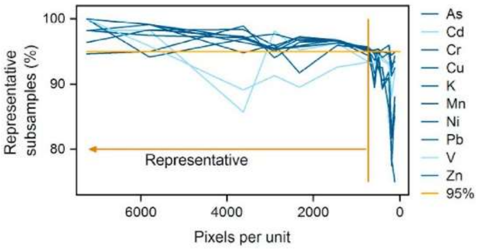

**Fig. 4.** Determination of the smallest representative subsample size due to nonhomogeneous material deposition on a filter. 5% of ZG 24. 1. 2017 filter sample was ablated for statistical analysis. The percentage of representative subsamples in the population is plotted against the unit size (*i.e.*, the number of pixels per unit). Each subsample analysed consisted of 3 randomly selected same-size units. The adequate confidence level for sampling was set at 95%, which infers that more than 95% of possible subsamples in the population are representative of the whole population. In contrast, the number of nonrepresentative subsamples (5%) represents the probability of wrong result when only one subsample is measured. With decreasing the size of units, the number of representative subsamples in the population also decreases. Some deviations can be observed in this regard, because the aspect ratio of different unit sizes was not the same due to practical reasons (the division of a population matrix on units is limited by dividers that can be applied on the population matrix).

observation the ablated craters on NIST RM 8785 seemed different from those on the filters from field used for the method development (Fig. S5). This indicates that NIST RM 8785 is not a true matrix-matched standard for the samples used in the current study and is, moreover, not suitable as a standard for LA-ICPMS.

Another calibration technique was thus applied. Three of the real samples (see Table S1 for their identity) were analysed by instrumental NAA ($k_0$-INAA) [51], which is a reference method for the determination of the elemental composition of a sample. These three differently loaded samples became our working standards as they were successfully applied for the calibration purposes. Seven elements (As, Fe, K, Mn, Sb, V, and Zn) were quantified by $k_0$-INAA after blank subtraction (*i.e.*, the correction for mass fractions from the filter). Other elements, such as Al, Ba, Co, Cr, Hf, rare earth elements, Mo, Na, Sc, Si, Th and U, were very close or below their LOD (*e.g.*, Cd, Ni, Se) due to insufficient nuclear reactions with target nuclei or because of the absence of a nuclear reaction from target's nuclei (*e.g.*, Tl, Pb).

As regards the LA-ICPMS analysis, measured elements and dwell times were all the same as in the calibration approach with NIST standard and are listed in Table S2. The data were treated according to the postprocessing protocol presented hereinabove (*i.e.*, spikes were eliminated prior to the statistical analysis). Comparison with the results without spike elimination was additionally made which is presented in Table S3. As already noted, such data can be used in great support of source apportionment, offering another insight into the PM composition as it identifies specific particles enriched with or depleted on some elements that are deposited on the filter. This is out of scope of this study but merits further investigation.

The results are presented in Fig. 5 and Table S4. To assess the accuracy of the developed LA-ICPMS method, the three different measurement techniques were also statistically compared: $k_0$-INAA as a reference method [52], the newly developed LA-ICPMS, and MW-ICPMS by the standard EN 14902:2005. The results for MW-ICPMS were obtained from ARSO, the government agency that monitors air quality with standardized methods on a daily basis. Three paired comparisons were made therefrom: MW-ICPMS vs. LA-ICPMS (n = 11), MW-ICPMS vs. $k_0$-INAA (n = 3), and LA-ICPMS vs. $k_0$-INAA (n = 3). A NPBPT was used for this purpose. With the Levene's test, equality of variances was first confirmed for all of the measured elements and comparisons (p-values are reported in Table S5), which increased the statistical power of NPBPT [41]. Note also that the comparison between $k_0$-INAA and LA-ICPMS is not totally uncorrelated since LA-ICPMS was calibrated based on $k_0$-INAA results. The results of NPBPT are listed in Table S6.

When MW-ICPMS and LA-ICPMS are compared with $k_0$-INAA, a statistically significant difference is only observed between MW-ICPMS and $k_0$-INAA concentrations for As, Fe and V (note p-values for Fe and Sb are very close to the significance level of $\alpha = 0.05$). On the other hand, the difference was never found significant in the pair LA-ICPMS and $k_0$-INAA. A statistically significant difference is also observed between MW-ICPMS and LA-ICPMS for As, Fe, and V, whereas all of the paired comparisons for Mn, Sb, and Zn can be considered statistically equal (caution with Sb, see note above). In most cases, the concentrations obtained with LA-ICPMS were higher than those measured with MW-ICPMS, which is expected due to possibly incomplete microwave digestion. These results confirm that LA-ICPMS produces as accurate results as $k_0$-INAA and performs better than MW-ICPMS, which is compromised by the unreproducible acid digestion step [5]. Moreover, LA-ICPMS proved itself more sensitive than MW-ICPMS, namely some element concentrations

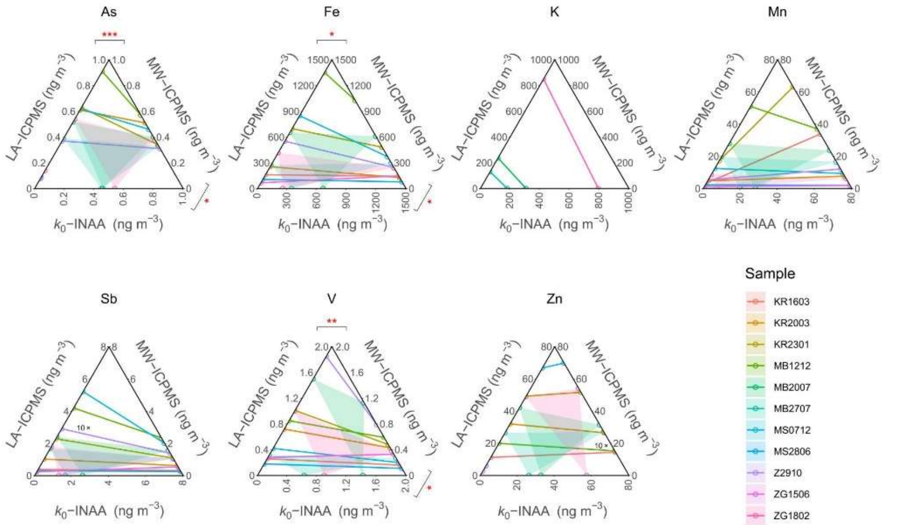

**Fig. 5.** A comparison between MW-ICPMS, $k_0$-INAA and LA-ICPMS. 11 differently loaded samples of known elemental composition by MW-ICPMS according to EN 14902:2005 were taken for analysis by LA-ICPMS applying the developed protocol. 3 samples were additionally analysed by $k_0$-INAA and used as working standards. Those 3 samples are presented with coloured triangles connecting three distinct points on each of the axis of a triangle plot. The other 8 samples were calibrated with use of the produced working standards and are considered real samples. For these, only the results for MW-ICPMS and LA-ICPMS are available and are depicted with lines connecting only two axes of a triangle plot. If the measured concentrations by both methods were the same, the connecting line would be horizontal. The concentrations of As and Zn were below the LOD of MW-ICPMS in three of the samples, which results in a lack of lines and leaves behind sole circles on LA-ICPMS axes. Two concentrations were divided by 10, which is stated by the corresponding lines. The stars denote statistically significant differences between the two methods that arise from that triangle corner (*$p < 0.05$; **$p \le 0.01$; ***$p \le 0.001$).

below the LOD of MW-ICPMS could be measured with LA (*i.e.*, As and Zn in three of the samples, Fig. 5).

## 4. Discussion

Given our interdisciplinary expertise in LA-ICPMS and atmospheric aerosol science, we recognized LA-ICPMS as a promising technique for the determination of the elemental composition of PM deposited on quartz fibre filters, which are commonly used in air quality monitoring. In this study, inhomogeneity of filter samples and not the method sensitivity was found determinant for filter sampling and the required sample size for analysis, which is not specifically considered in the standard EN 14902:2005. The main issue that needs to be addressed before the developed protocol in Fig. 6 can be widely exploited is the commercial availability of matrix-matched standards with specified elemental composition and similar ablation properties to real samples (*i.e.*, PM on quartz fibre filter).

To prove the concept, a few high-volume quartz fibre filter samples from the field were standardized by $k_0$-INAA for the need of this study. This, however, cannot be a part of a standard protocol for routine air quality monitoring. Moreover, NAA is not suitable for the determination of some important elements, *e.g.*, Pb due to their inactivity for neutron activation. Therefore, standardization supported by other analytical techniques as common for NIST standard reference materials (SRM) is necessary for the full exploitation of LA-ICPMS capabilities. NIST already offers reference materials of air particulate matter on filter media, such as PM2.5 on a polycarbonate filter membrane certified for its elemental composition (SRM 2783) and PM2.5 collected on a quartz-fibre filter with the certified carbon content (RM 8785). This makes us confident that if demand arises from the standardization of the proposed analytical technique for PM analysis, NIST or any other producer of standard materials will respond in its full support and offer suitable commercial standards in a reasonable time.

In this work, we compare the results of the newly developed method with the standard method by MW-ICPMS (EN 14902:2005) and a reference method by $k_0$-INAA. LA-ICPMS roughly gave comparable results to the other two analytical techniques; however, a wider study is necessary to validate its performance in this regard. In most cases, concentrations were higher than those determined by MW-ICPMS, which was attributed to incomplete acid digestion according to the latter method. LA-ICPMS turned out to be more sensitive than MW-ICPMS (no sample dilution and impurities in used chemicals increasing the noise) and requires about 50-times less sample without any pretreatment prior to the analysis. With this, the measurement time is substantially shortened (less than 30 min per sample compared to 3 h for the standard procedure) and the burden for the environment is minimized (no chemical waste is produced). Moreover, more sample is kept available for complementary analyses which is typical in atmospheric chemistry research. LA-ICPMS has a wide dynamic range and is capable of monitoring a whole palette of elements simultaneously (we successfully measured 19 potentially important elements in PM: Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Tl, V, and Zn), whereas the standard method is only certified for Pb, Cd, As, and Ni. Recoveries of other elements during microwave digestion can be sometimes incomplete.

During the study, however, we encountered two elements that could not be simply measured with the LA-ICPMS setup used. Selenium due to very high background (*i.e.*, 50 times higher than the next highest background measured for K; Fig. S6a), which is most likely caused by interferences that emerge during the measurement ($^{40}Ar^{38}Ar+$ and $^{38}Ar^{40}Ca$ + are possible polyatomic interferences for $^{78}Se$) [53]. Consequently, concentrations of Se in our samples were too low to be differentiated from gas blank even at very long dwell times (0.5 s). This problem can be solved with use of a triple quadrupole ICPMS instrument, which eliminates polyatomic interferences more efficiently and thereby lowers the instrument background signal improving the LOD

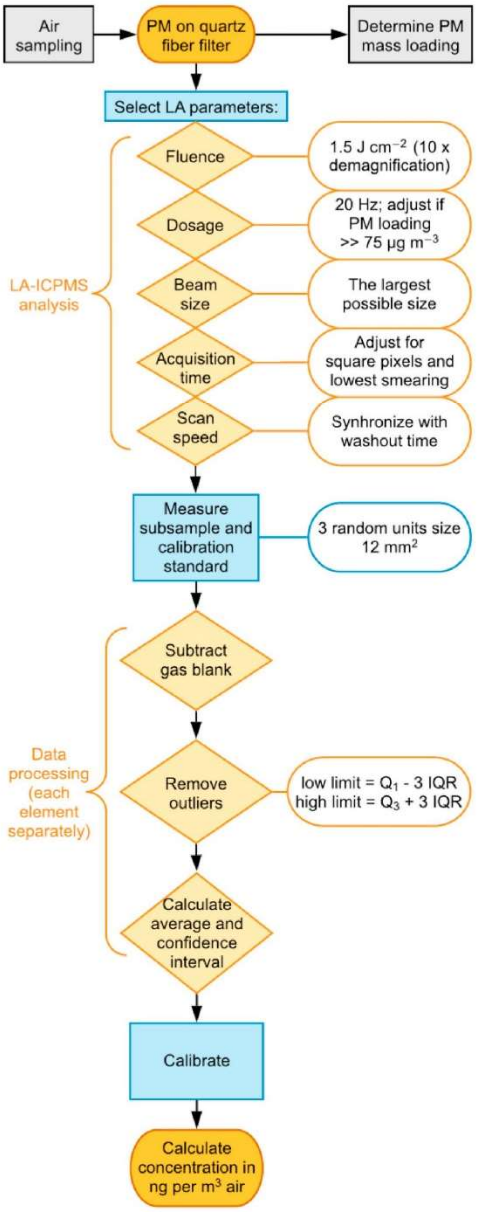

**Fig. 6.** Schematic of the developed protocol for the determination of elemental composition of PM on quartz fibre filters by using LA-ICPMS. Samples can be low- or high-volume, whereas instrument parameters (dosage) may have to be adjusted in regard to the thickness of PM deposit on a filter.

substantially. It is, however, a significantly more expensive instrument and may not be the first choice for routine monitoring.

The second problematic element is mercury; every time, its stability during the ablation was questioned. For the time of ablation, the concentration of mercury was always drastically decreasing (Fig. S6b), which was observed many times independently. We attributed the observed effect to Hg evaporation during the ablation. A spiked thin layer of non-metal coating over the filter would theoretically prevent its evaporation during ablation and enable its determination in PM filter samples by the developed method. This, however, was not the scope of this study.

For any instrument used for routine analyses it is paramount to offer high-throughput and be affordable. In comparison to the conventional method by acid digestion, where industrial-type microwave furnace and ICPMS are required, we promote a new method by LA-ICPMS where LA system replaces microwave furnace in a sample preparation step, which can double initial investment in the equipment. Nevertheless, not being interested in supreme resolution, lasers for this type of analysis don't need to be state-of-the-art fast aerosol delivery systems. We expect this will substantially reduce the connected costs once the demand for such systems arises. At the same time, the sensitivity of the instrument for multiple elements will also improve due to longer washout times (allowing for longer acquisition times), which is advantageous in the case of PM ultratrace analysis. Moreover, low wavelengths and high power lasers such as the one used in this study are preferably used for the ablation of hard materials (*e.g.*, quartz), which in our case only adds to the background noise. Therefore, we also believe that lasers with higher wavelengths and lower power can be successfully applied for PM analysis (*e.g.*, 213 nm), which is again in favour of the LA system cost. However, there is some progress in instrument development expected before the method can be routinely used, suggesting i) increased laser beam sizes and ii) the development of autosamplers or ablation cells with customized filter mount and low volume allowing fast purge times, both improving the speed of analysis and minimizing related laboratory work.

## 5. Conclusions

In this paper we have developed an analytical method for determining the elemental composition of PM collected on quartz fibre filters, which are most widely used in routine air quality monitoring by environment agencies all around the world. The newly developed method is shown to be highly advantageous to the established method used for the purpose in several aspects. It eliminates the laborious sample preparation step with microwave digestion. This further results in a more precise measurement of a multitude of elements, while only four elements can be measured with certainty by the established method. The use of laser ablation as a sampling method eliminates the production of toxic waste, which qualifies the developed method as a green analytical method and importantly contributes to the environmental protection that is often overlooked due to higher purposes. Moreover, according to the developed protocol, a minute amount of sample is required, hence the remaining sample can be used for other complementary analyses, such as OC/EC, organic analysis, and ions. The results obtained with the developed LA-ICPMS method were compared to the commonly used MW-ICPMS and $k_0$-INAA as a reference method for the determination of the elemental composition of a sample, and we have shown by use of statistical analysis that the results by the developed method have no significant differences toward $k_0$-INAA, whereas there were some differences toward the commonly applied MW-ICPMS. This is not surprising because it has been reported previously that microwave assisted digestion is not complete for most of elements and consequently, the measurements by this method are underestimated. Although the advocated LA-ICPMS method is accurate and fast, there is still room for improvement via instrumental development to adjust dedicated laser ablation systems, which is elaborated herein. It is especially paramount for its wide application that suitable matrix-matched standards become commercially available.

## Author contributions

Monika Ogrizek, Investigation, Formal analysis, Writing – original draft, Visualization. Radojko Jaćimović, Investigation. Martin Šala, Conceptualization, Methodology, Writing – original draft, Supervision, Funding acquisition. Ana Kroflič, Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2021.122110.

## References

[1] J. Lelieveld, J.S. Evans, M. Fnais, D. Giannadaki, A. Pozzer, The contribution of outdoor air pollution sources to premature mortality on a global scale, Nature 525 (7569) (2015) 367–371.

[2] J.D. Stanaway, et al., Global, regional, and national comparative risk assessment of 84 behavioural, environmental and occupational, and metabolic risks or clusters of risks for 195 countries and territories, 1990-2017: a systematic analysis for the Global Burden of Disease study 2017, Lancet 392 (2018) 1923–1994, 10159.

[3] Y. Ou, J.J. West, S.J. Smith, C.G. Nolte, D.H. Loughlin, Air pollution control strategies directly limiting national health damages in the US, Nat. Commun. 11 (1) (2020) 957.

[4] H. Yue, C. He, Q. Huang, D. Yin, B.A. Bryan, Stronger policy required to substantially reduce deaths from PM2.5 pollution in China, Nat. Commun. 11 (1) (2020) 1462.

[5] J. Aldabe, C. Santamaria, D. Elustondo, E. Lasheras, J.M. Santamaria, Application of microwave digestion and ICP-MS to simultaneous analysis of major and trace elements in aerosol samples collected on quartz filters, Anal. Methods 5 (2) (2013) 554–559.

[6] R. Beelen, et al., Natural-cause mortality and long-term exposure to particle components: an analysis of 19 European cohorts within the multi-center ESCAPE project, Environ. Health Perspect. 123 (6) (2015) 525–533.

[7] S. Goix, G. Uzu, P. Oliva, F. Barraza, A. Calas, S. Castet, D. Point, J. Masbou, J. L. Duprey, C. Huayta, J. Chincheros, J. Gardon, Metal concentration and bioaccessibility in different particle sizes of dust and aerosols to refine metal exposure assessment, J. Hazard Mater. 317 (2016) 552–562.

[8] E. Lequy, J. Siemiatycki, S. Leblond, C. Meyer, S. Zhivin, D. Vienneau, K. de Hoogh, M. Goldberg, M. Zins, B. Jacquemin, Long-term exposure to atmospheric metals assessed by mosses and mortality in France, Environ. Int. 129 (2019) 145–153.

[9] P. Wang, Q.H. Zhang, Y.M. Li, J. Matsiko, Y. Zhang, G.B. Jiang, Airborne persistent toxic substances (PTSs) in China: occurrence and its implication associated with air pollution, Environ. Sci.-Process Impacts 19 (8) (2017) 983–999.

[10] M.G. Lionetto, M.R. Guascito, R. Caricato, M.E. Giordano, A.R. De Bartolomeo, M. P. Romano, M. Conte, A. Dinoi, D. Contini, Correlation of oxidative potential with ecotoxicological and cytotoxicological potential of PM10 at an urban background site in Italy, Atmosphere 10 (12) (2019) 10.

[11] EPA, Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, United States Environmental Protection Agency, 1999.

[12] CEN, Ambient air quality, in: Standard Method for the Measurement of Pb, Cd, AS, and Ni in the PM 10 Fraction of Suspended Particulate Matter, vol. 2005, CEN, 2005.

[13] S. Cakmak, R. Dales, L.M. Kauri, M. Mahmud, K. Van Ryswyk, J. Vanos, L. Liu, P. Kumarathasan, E. Thomson, R. Vincent, S. Weichenthal, Metal composition of fine particulate air pollution and acute changes in cardiorespiratory physiology, Environ. Pollut. 189 (2014) 208–214.

[14] K.S. Egorova, V.P. Ananikov, Toxicity of metal compounds: knowledge and myths, Organometallics 36 (21) (2017) 4071–4090.

[15] X. Hu, Y. Zhang, Z.H. Ding, T.J. Wang, H.Z. Lian, Y.Y. Sun, J.C. Wu, Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China, Atmos, Environ. Times 57 (2012) 146–152.

[16] Y. Shang, M.Y. Wu, J.Z. Zhou, X. Zhang, Y.F. Zhong, J. An, G.R. Qian, Cytotoxicity comparison between fine particles emitted from the combustion of municipal solid waste and biomass, J. Hazard Mater. 367 (2019) 316–324.

[17] Y. Yuan, Y. Wu, X.L. Ge, D.Y. Nie, M. Wang, H.T. Zhou, M.D. Chen, In vitro toxicity evaluation of heavy metals in urban air particulate matter on human lung epithelial cells, Sci. Total Environ. 678 (2019) 301–308.

[18] S.W. Wu, F.R. Deng, Y. Hao, M. Shima, X. Wang, C.J. Zheng, H.Y. Wei, H.B. Lv, X. L. Lu, J. Huang, Y. Qin, X.B. Guo, Chemical constituents of fine particulate air pollution and pulmonary function in healthy adults: the healthy volunteer natural relocation study, J. Hazard Mater. 260 (2013) 183–191.

[19] C.A. Belis, et al., Evaluation of receptor and chemical transport models for PM10 source apportionment, Atmos. Environ-X 5 (2020) 23.

[20] R.J.C. Brown, K.E. Jarvis, B.A. Disch, S.L. Goddard, E. Adriaenssens, N. Claeys, Comparison of ED-XRF and LA-ICP-MS with the European reference method of acid digestion-ICP-MS for the measurement of metals in ambient particulate matter, Accred Qual. Assur. 15 (9) (2010) 493–502.

[21] S. Gligorovski, J.T. Elteren, I. Grgić, A multi-element mapping approach for size-segregated atmospheric particles using laser ablation ICP-MS combined with image analysis, Sci. Total Environ. 407 (1) (2008) 594–602.

[22] Y.K. Hsieh, L.K. Chen, H.F. Hsieh, C.H. Huang, C.F. Wang, Elemental analysis of airborne particulate matter using an electrical low-pressure impactor and laser ablation/inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 26 (7) (2011) 1502–1508.

[23] R. Jaworski, T. Wroblewski, E. Hoffmann, Laser ablation studies of solid aerosols on the Baltic coast, Oceanologia 46 (3) (2004) 333–345.

[24] T. Okuda, J. Kato, J. Mori, M. Tenmoku, Y. Suda, S. Tanaka, K.B. He, Y.L. Ma, F. Yang, X.C. Yu, F.K. Duan, Y. Lei, Daily concentrations of trace metals in aerosols in Beijing, China, determined by using inductively coupled plasma mass spectrometry equipped with laser ablation analysis, and source identification of aerosols, Sci, Total Environ 330 (1–3) (2004) 145–158.

[25] T. Okuda, M. Tenmoku, J. Kato, J. Mori, T. Sato, R. Yokochi, S. Tanaka, Long-term observation of trace metal concentration in aerosols at a remote island, Rishiri, Japan by using inductively coupled plasma mass spectrometry equipped with laser ablation, Water Air Soil Pollut. 174 (1–4) (2006) 3–17.

[26] M.S. Robinson, I. Grgić, V.S. Šelih, M. Šala, M. Bitsui, J.T. van Elteren, Laser ablation ICP-MS of size-segregated atmospheric particles collected with a MOUDI cascade impactor: a proof of concept, Atmos. Meas. Tech. 10 (5) (2017) 1823–1830.

[27] S. Rovelli, W. Nischkauer, D.M. Cavallo, A. Limbeck, Multi-element analysis of size-segregated fine and ultrafine particulate via laser ablation-inductively coupled plasma-mass spectrometry, Anal. Chim. Acta 1043 (2018) 11–19.

[28] S. Tanaka, N. Yasushi, N. Sato, T. Fukasawa, S.J. Santosa, K. Yamanaka, T. Ootoshi, Rapid and simultaneous multi-element analysis of atmospheric particulate matter using inductively coupled plasma mass spectrometry with laser ablation sample introduction, J. Anal. At. Spectrom. 13 (2) (1998) 135–140.

[29] C.F. Wang, C.J. Chin, S.K. Luo, L.C. Men, Determination of chromium in airborne particulate matter by high resolution and laser ablation inductively coupled plasma mass spectrometry, Anal. Chim. Acta 389 (1–3) (1999) 257–266.

[30] C. Ludke, E. Hoffmann, J. Skole, Comparative studies on metal determination in airborne particulates by LA-ICP-MS and furnace atomization non-thermal excitation spectrometry, Fresenius' J. Anal. Chem. 350 (4–5) (1994) 272–276.

[31] X.X. Tang, Y. Qian, Y.C. Guo, N.N. Wei, Y.L. Li, J. Yao, G.H. Wang, J.F. Ma, W. Liu, Analysis of atmospheric pollutant metals by laser ablation inductively coupled plasma mass spectrometry with a radial line-scan dried-droplet approach, Spectroc. Acta Pt. B Atom. Spectr. 138 (2017) 18–22.

[32] HyperLab 2002 System, Installation and Quick Start Guide, HyperLabs Software, Budapest, Hungary, 2002.

[33] Kayzero for Windows (KayWin®), User's Manual for Reactor Neutron Activation Analysis (NAA) Using the $k_0$ Standardization Method, 2005.

[34] R. R Core Team, A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna (Austria), 2019.

[35] R.J. Hijmans, raster: geographic data analysis and modeling, R package version 2 (2019) 8–19.

[36] R. Bivand, T. Keitt, Bindings for the 'geospatial' data abstraction library, R package version 1 (2019) 4.

[37] H. Wickham, Reshaping data with the reshape package, J. Stat. Software 21 (12) (2007) 1–20.

[38] J. Fox, S. Weisberg, An R Companion to Applied Regression, second ed., Sage, Thousand Oaks (CA), 2011.

[39] H. Wickham, ggplot2: Elegant Graphics for Data Analysis, Springer-Verlag New York2016.

[40] N.E. Hamilton, M. Ferry, ggtern: ternary diagrams using ggplot2, J. Stat. Software 87 (CN3) (2018) 1–17.

[41] A.K. Dwivedi, I. Mallawaarachchi, L.A. Alvarado, Analysis of small sample size studies using nonparametric bootstrap test with pooled resampling method, Stat. Med. 36 (14) (2017) 2187–2205.

[42] S.J.M. Van Malderen, A.J. Managh, B.L. Sharp, F. Vanhaecke, Recent developments in the design of rapid response cells for laser ablation-inductively coupled plasma-mass spectrometry and their impact on bioimaging applications, J. Anal. At. Spectrom. 31 (2) (2016) 423–439.

[43] J.T. van Elteren, M. Šala, V.S. Šelih, Perceptual image quality metrics concept in continuous scanning 2D laser ablation-inductively coupled plasma mass spectrometry bioimaging, Anal. Chem. 90 (9) (2018) 5916–5922.

[44] J.T. van Elteren, V.S. Šelih, M. Šala, Insights into the selection of 2D LA-ICP-MS (multi)elemental mapping conditions, J. Anal. At. Spectrom. 34 (9) (2019) 1919–1931.

[45] EEA, Air Quality in Europe — 2019 Report, European Environment Agency, Luxembourg, 2019.

[46] G. Steinhoff, O. Haupt, W. Dannecker, Fast determination of trace elements on aerosol-loaded filters by X-ray fluorescence analysis considering the inhomogeneous elemental distribution, Fresenius' J. Anal. Chem. 366 (2) (2000) 174–177.

[47] R.J.C. Brown, K.E. Jarvis, B.A. Disch, S.L. Goddard, A.S. Brown, Spatial inhomogeneity of metals in particulate matter on ambient air filters determined by LA-ICP-MS and comparison with acid digestion ICP-MS, J. Environ. Monit. 11 (11) (2009) 2022–2029.

[48] K. Widziewicz, K. Loska, W. Rogula-Kozlowska, Metals distribution on the surface of quartz fiber filters used for particulate matter collection, Arch. Environ. Protect. 41 (4) (2015) 3–10.

[49] D. Metarapi, M. Šala, K. Vogel-Mikuš, V.S. Šelih, J.T. van Elteren, Nanoparticle analysis in biomaterials using laser ablation-single particle-inductively coupled plasma mass spectrometry, Anal. Chem. 91 (9) (2019) 6200–6205.

[50] M.D. Montano, J.W. Olesik, A.G. Barber, K. Challis, J.F. Ranville, Single particle ICP-MS: advances toward routine analysis of nanomaterials, Anal. Bioanal. Chem. 408 (19) (2016) 5053–5074.

[51] R. Jaćimović, B. Smodiš, T. Bučar, P. Stegnar, $k_0$-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software, J. Radioanal. Nucl. Chem. 257 (3) (2003) 659–663.

[52] R.R. Greenberg, P. Bode, E.A. De Nadai Fernandes, Neutron activation analysis: a primary method of measurement, Spectroc, Acta Pt. B 66 (3–4) (2011) 193–241.

[53] T.W. May, R.H. Wiedmeyer, A table of polyatomic interferences in ICP-MS, Atom. Spectros 19 (5) (1998) 150–155.

## 3.3 Manuscript 3: Evaluation of 213 nm Laser as an Affordable Alternative for the Green Elemental Characterization of Particulate Matter on Quartz Fibre Filters by Laser Ablation ICPMS

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The method for the elemental determination of PM developed in the previous article was based on an excimer 193 nm LA system, which is available at the location of candidate's workplace. However, this powerful LA system is quite an initial investment and a cheaper alternative, which we recognized suitable for our application, would definitely ease the transition to the green analytical method in monitoring agencies and make the method more affordable in general. One such option is a solid state 213 nm LA system, which is probably the second most used LA system in research. As LA systems with different wavelengths behave differently regarding the optimal instrumental parameters, coupling with a sample, elemental fractionation, *etc.*, the developed method could not be simply generalized to the different wavelength. In collaboration with colleagues at the Masaryk University in Brno, the LA method for the elemental determination of PM collected on quartz fiber filters was adapted and optimized for a more affordable 213 nm LA system.

The PM samples used for the optimization were collected during routine air-quality monitoring and were again donated by ARSO, together with the data on their elemental concentrations determined with the standard MW/ICPMS method. After the optimization of measurement parameters (*i.e.* laser beam size and scan speed, fluence, and dosage), eight PM samples from different seasons, a blank filter, and typical glass standards for LA (NIST SRM 610 and 612) were measured with 213 nm and 193 nm LA systems, using the optimal set of parameters for each instrument, to compare their performance. Blank filter ablation and disturbances due to the contained impurities were studied, PM samples were analyzed and the results compared, sensitivity and LODs, as well as the ability to determine different elements, were investigated for both set-ups. The calibration procedure remained a problem, therefore, calibration was performed with a leave-one-out cross-validation procedure based on the measured samples, using elemental data gained from the MW/ICPMS analysis, which fit the purpose of this research. Statistical comparison of methods was performed with the paired t-test or the non-parametric alternative Wilcoxon test, dependent on the results of the Shapiro-Wilk test evaluating the assumption of normality. Moreover, when comparing all three methods (213 and 193 nm LA system, and MW/ICPMS), analysis of variances (ANOVA) or the non-parametric Friedman test were applied. For sensitivity comparison, visual evaluation of the background noise (*i.e.* gas blank), low concentration sample, and NIST SRM were made by distinguishing features in images and comparing pixel counts.

As a result, we found out that 213 nm LA ablated more blank filter material, which released more impurities from quartz fiber matrix. Special attention in this regard is specifically advised when measuring Ni and Mo with 213 nm and in the case of Cr with both LA systems. Statistical analysis of the three methods did not reveal any evidence of the difference among the methods in any of the elements, showing that the tested LA systems perform comparably well in terms of accuracy. On the other hand, in the case of the 213 nm LA system, the sensitivity was poorer for Ca, Cd, Pb, Sb, and Sn; LOD was higher for Ba, Cd, and Pb; and Tl could not be determined at all, compared to the 193 nm LA system.

Although 213 nm LA system exhibited poorer performance for certain elements, LODs and working ranges are still assessed sufficient for the current legislation and comparable to the standard method, providing additional benefits in terms of multi-element and green determination of PM. The 193 nm LA system might have some advantages in the determination of a longer list of elements in PM, which is especially useful in source apportionment studies, but for everyday monitoring purposes we find 213 nm LA system suitable and a valid, affordable alternative with the potential to replace the standard MW/ICPMS method in the future.

# Evaluation of 213 nm laser as an affordable alternative for the green elemental characterization of particulate matter on quartz fibre filters by laser ablation ICPMS

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## Abstract

Airborne particles, denoted as particulate matter (PM), are one of major environmental pollutants. Particles smaller than 10 µm ($PM_{10}$) penetrate into the human lungs during breathing and exert damage by physical and chemical mechanisms. PM mass concentration in the air as well as major toxicants contained are thus regulated by relevant directives all around the world and their continuous monitoring is prescribed. Elemental composition of PM is one of the most often measured air-quality parameters and the standard method for its determination produces huge amounts of toxic chemical waste. Sustainable alternatives are thus sought for, such as laser ablation inductively coupled plasma mass spectroscopy (LA-ICPMS), which allows for the direct analysis of PM collected on a filter without the microwave-assisted extraction step prior to the analysis with ICPMS. In this work we evaluated the performance of 213 nm Nd:YAG laser system (LA213) compared to the more powerful 193 nm excimer laser (LA193) for this application, in order to facilitate replacement of the standard method with a new, greener one. We show that LA213 produces good results when operated under optimized instrument conditions, which were in fact very similar to the LA193 system. Sensitivity for some elements was, however, a bit poorer, but this can be overcome with additional fine-tuning, if necessary. Wrapping-up our thorough evaluation we can conclude that the more affordable LA213 is suitable for air-quality monitoring purposes.

**Keywords:**

PM, trace elements, metal concentration, sustainable, air quality monitoring, LA-ICPMS

## 1 Introduction

Particulate matter (PM) is one of the major air pollutants threatening the environment and human population (World Health Organization, WHO). PM is responsible for millions of deaths every year, among others causing pulmonary and cardiovascular diseases, and cancer (Lelieveld et al., 2015; Roy et al., 2016; Zhang et al., 2022). On the other hand, PM contributes to climate change by interfering with sun and Earth radiation pathways (Fuzzi et al., 2015).

The excess of PM which disrupts the natural balance is emitted by anthropogenic activities, such as traffic, industry, and biomass burning (Chatoutsidou et al., 2019; Karagulian et al., 2015; Trippetta et al., 2016; Tsiouri et al., 2015). Although, due to its nanoparticle nature, PM is harmful on its own, different sources produce distinctive particle structures and compositions, which finally determine the level of PM toxicity (Goix et al., 2016; Hu et al., 2012). Typically, PM is composed of inorganic ions, organic carbon, elemental carbon, crustal elements, and trace metals, some of these being known toxicants, such as polycyclic aromatic hydrocarbons (PAH) and particular trace elements. Besides PAH, airborne As, Cd, Ni, and Pb are regulated by the EU Commission (Directive 2004/107/EC and 2008/50/EC) prescribing their limit values and assuring safe living conditions along with limiting their influence on the environment. Moreover, reduction of national emissions of some other trace elements has also been commanded to date (Directive (EU) 2016/2284).

Accordingly, a standard method for the element determination in PM is prescribed (EN14902:2005). It is certified for the regulated four elements, although monitoring of Cr, Cu, Se, and Zn has also been ordered in Directive (EU) 2016/2284 due to their adverse effects to human health and the environment (Jaishankar et al., 2014; Tchounwou et al., 2012). The main disadvantage of the standard method is the sample preparation step. Microwave assisted digestion (MW) with concentrated nitric acid and hydrogen peroxide is prescribed prior to the analysis with inductively coupled plasma mass spectroscopy (ICPMS) or graphite furnace atomic absorption spectrometry (GF-AAS). However, the protocol does not result in a complete digestion of quartz fibre filter and several authors report that accurate multielement determination in various PM matrixes is not guaranteed by this method (Aldabe et al., 2013; Swami et al., 2001). Moreover, MW is an additional step to the analysis, which increases the likelihood of sample contamination and/or loss of volatile elements. It is time consuming and requires high-purity reagents to assure sufficiently low limits of detection (LOD). The required reagents not only raise the cost of analysis but also end up as a toxic waste, which is not negligible if considering every-day monitoring at numerous stations around the world (Bai et al., 2022; Gerboles and Buzica, 2008; Ogrizek et al., 2022; Pant et al., 2019; Rovelli et al., 2018; Wang et al., 1998).

A green solution to this problem is to use analytical techniques capable of determining elemental composition directly on the solid PM samples (Gini et al., 2021). Relevant techniques which all have their advantages and drawbacks are described in detail in our recent review paper (Ogrizek et al., 2022), in which energy dispersive XRF (EDXRF) and LA-ICPMS have been recognized as most promising to replace the standard method currently in use. LA-ICPMS generally provides lower LODs than EDXRF and thus allows to detect and quantify more elements especially in low-polluted samples, which is often necessary when performing source apportionment studies. Moreover, LA-ICPMS can be directly applied to quartz fibre filters, the most universal and widely used filter matrix including in environment agencies, since quartz withstands high temperatures needed for complementary organic and elemental carbon analyses.

While the standard MW/ICPMS and the proposed green LA-ICPMS method can utilise identical ICPMS instruments, allowing monitoring agencies to keep exploiting the original ICPMS function for liquid environmental samples (*e.g.* ground water samples), save on space and eliminate/limit the need for additional educated personnel, a new LA system is indeed a bigger initial investment compared to a microwave owen. The recently developed method for the elemental determination of PM uses a 193 nm excimer LA system (LA193) (Ogrizek et al., 2021); however, more affordable alternatives also exist on the market, as is 213 nm Nd:YAG (LA213). Nevertheless, different LA systems and wavelengths do not couple with material in the same way, which needs to be explored for the case of PM samples.

While excimer LA193 systems are characterized by homogeneous energy distribution inside the laser beam generating evenly flat craters, solid state LA213 systems are known for irregularities in laser energies inside the laser beam, resulting in a more undulating crater base (Gilbert et al., 2014). For this reason, in analytics, LA193 systems are usually preferred. Besides, less fractionation effects are observed in the case of high energy lasers compared to the higher wavelength lasers, which improves analytical accuracy especially when homogeneous, matrix-matched standards are not available for calibration. Another effect arising from the different wavelengths used for laser ablation is distinct size distribution of particles generated during the ablation, which are generally moved towards the smaller size range (< 150 nm) in the case of LA193 compared to the LA wavelengths above 200 nm (particle sizes of up to 1 µm are anticipated; both sizes are related to the ablation of NIST 610 series silicate glasses) (Guillong et al., 2003). Larger particle sizes can be problematic, since they tend to deposit close to the ablation crater and may not get transported to the ICPMS at all. Furthermore, even if these particles enter the plasma, their conversion to ions may be incomplete, which consequently influences the sensitivity of the measurement. It has been further shown that sample characteristics, *i.e.* sample transparency also influence particle size distribution and stability of the signal (Gonzalez et al., 2002; Guillong and Gunther, 2002). While LA193 performed better in the case of more transparent samples (*e.g.* NIST 612 and 614), for more opaque NIST 610 the particle size distribution and signal stability were similar for LA193 and LA213 systems (Guillong et al., 2003).

As PM samples are opaque, beige to dark brown in colour, no differences in fractionation effects due to ablation are expected between LA193 and LA213. Nevertheless, another fractionation effect could be due to different laser irradiances or power densities, which can cause sample heating or melting (Wohlgemuth-Ueberwasser and Jochumb, 2015). The 193 nm excimer and 213 nm Nd:YAG are both nanosecond lasers, where melting was observed in the past compared to the femtosecond lasers (Luo et al., 2020; Wohlgemuth-Ueberwasser and Jochumb, 2015). If similar pulse width (4–5 ns) and laser energy density were used, LA213 produced more melting during the ablation of sulphides compared to LA193 (Wohlgemuth-Ueberwasser and Jochumb, 2015). Notwithstanding, with different pulse width and fluence applied in the ablation of alloy steels (3 ns with fluences 3.5–12.1 J cm$^{-2}$ for LA213 and 15 ns with fluences 5.1–14.5 J cm$^{-2}$ for LA193), the least melting was observed in the case of short pulse width and low fluence with LA213 (Luo et al., 2020). Note, however, that with LA213 systems higher fluence is usually needed for comparable ablation to the LA193 (*e.g.* 4.2 vs 2.7 J cm$^{-2}$ for sulphide analysis (Gilbert et al., 2014), or 15 vs 5 J cm$^{-2}$ for typical reference materials (RM) as are NIST 610, GSE-1G, MACS-3, and STDP5 (Jochum et al., 2014), for LA213 vs LA193, respectively).

In this study we investigate utilisation of the 213 nm Nd:YAG LA-ICPMS for the determination of the elemental composition of PM collected on quartz fibre filters. A new method is developed for this particular application and compared to the already existing 193 nm excimer LA-ICPMS (Ogrizek et al., 2021). The potential of the more affordable LA213 system for air-quality monitoring purposes is specifically addressed, which would facilitate the worldwide transition to a more sustainable analysis in the future. Sensitivity of both methods in respect to different elements is explored and applicability of the new method is discussed, considering also the initial investment in the equipment, which can be critical especially in research, while for environment agencies the return of investment is faster due to circumventing the laborious pre-extraction step (>3 h per sample set) and huge amounts of toxic waste (100 ml per sample).

## 2 Experimental section

### 2.1 Samples and standard materials

Ambient $PM_{10}$ samples were donated by the Slovenian Environment Agency (ARSO) and were collected during their routine monitoring according to the current EU legislation (EN12341:2014 and EN14902:2005). Sampling was performed by a high volume sampler (Digitel DHA-80 Aerosol Sampler, Switzerland) for 24 h with a flow rate of 500 L $min^{-1}$ on quartz fibre filters (PALL, USA; filter diameter 150 mm). The samples were collected in Maribor, Slovenia (111,000 inhabitants), representative of an urban environment with traffic and biomass burning as two major pollution sources. Samples from various seasons thus provided different filter loadings and analyte concentrations.

Trace elements in glass SRM 610 and 612 (NIST, USA) were used for testing the intraday stability of the instruments and comparison of sensitivity between LA systems. Pristine quartz fibre filters (PALL, USA) were used as filter blanks.

### 2.2 LA-ICPMS instruments

LA is a special process used to introduce solid samples to ICPMS for analysis. Since no sample pre-treatment is required, $PM_{10}$ samples were simply cut and mounted to a microscopic glass with a double sided tape (Scotch, USA) and put into a holder for analysis. Two LA systems using different laser generators and wavelengths were compared: (i) 193 nm nanosecond excimer LA system (193 nm ArF*; Analyte G2, Teledyne Photon Machines Inc., Bozeman, MT; later referred as LA193) at the National Institute of Chemistry, Slovenia, and (ii) 213 nm nanosecond solid state LA system (Nd:YAG, LSX 213 G2; Teledyne Photon Machines Inc., Bozeman, MT; later referred as LA213) at the Masaryk University, Czech Republic. 2-volume ablation cell with He as a carrier gas was used in both cases (HelEx II ablation cell for LA193 and HelEx for LA213). Carrier gas flow rate was 0.5 and 0.6 L $min^{-1}$ for the cup, respectively, and

0.3 L min$^{-1}$ for the cell (in both cases). The same type of a quadrupole ICPMS instrument (Agilent 7900, Agilent Technologies, Santa Clara, CA) was used for detection in both cases, with Ar as a makeup gas (0.8 L min$^{-1}$).

Twenty elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Ti, Tl, V, and Zn) were measured simultaneously with the total acquisition time of 0.5 s and element specific dwell times as listed in Table S1.

### 2.2.1 Parameter optimization

Although it is known that each airborne particle is unique, the focus of the current paper is on the analysis of bulk concentrations of trace elements in PM deposited on collection filters, as required by the legislation. Therefore, instrument parameters were optimized to measure large sample area in a short amount of time, and to ablate the majority of the PM deposited on the filter rather than obtaining a perfect LA image. Optimization of LA193 parameters is described in Ogrizek et al. (2021) and LA213 optimization was approached in a similar way.

Based on our previous knowledge, ablation was performed using the adjacent line-scan mode, with the largest beam size LA system is capable to produce, and scan speed calculated to provide square pixels with a minimal smear. Acquisition time was synchronized with the washout time of the used ablation cell and was similar in both LA systems.

Three parameters were optimized experimentally: fluence (0.9–8.6 J cm$^{-2}$), scan speed and repetition rate that correspond to dosage 2–20 were used with the LA213 (details in Table S2). During fluence optimization, two ablation passes were repeated over the same ablation line to determine the amount of residual PM on a filter. Due to limitations of the maximum repetition rate (20 Hz), dosage optimization had to be performed at two different scan speeds (250 µm s$^{-1}$ for dosages 2–10 and 125 µm s$^{-1}$ for dosages 12–20); therefore, a sum of pixels was used to compare the different dosages instead of an average as used in the fluence optimization. An area of 3.15 mm² was ablated for every tested parameter and experiments were repeated on four different PM samples (two summer and two winter samples) for all twenty elements.

### 2.2.2 Sample Analysis

The set of optimized LA213 parameters was first applied to the ablation of a blank filter, to study the potential influence of impurities to the PM composition determination.

Eight ambient $PM_{10}$ samples with different PM loadings and elemental concentrations (Table S3) were further measured by both LA systems using the optimal sets of parameters to compare instrument performance. Due to the inhomogeneity of PM material deposited on a filter, every time a 3 × 12 mm² filter area was randomly ablated to be representative of the whole PM filter as has been recently shown in Ogrizek et al. (2021).

The samples were quantified based on known elemental concentrations from the standard MW/ICPMS analysis (data received by the Slovenian Environment Agency) with a leave-one-out cross-validation procedure (LOOCV). When heteroscedastic characteristics of the data drastically influenced the determination of low concentration samples, a weighted ($x^{-1}$) linear model was used (*i.e.* for As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Rb, V, Zn).

Differences between LA systems were statistically evaluated with the paired t-test or the paired Wilcoxon test in the case of elements where the assumption of normality was not met (the latter was assessed with the Shapiro-Wilk test). Furthermore, all three determination methods (LA193, LA213, MW/ICPMS) were compared with the repeated measures ANOVA or its appropriate non-parametric alternative (*i.e.* Friedman test). For visual representation of uncalibrated results the data were normalized (1) to allow for the comparison of different scales.

$$x_{normalized} = (x - average)\ stdev^{-1} \qquad (1)$$

Statistical analysis was performed in software R and raster, data.table, reshape2 (Wickham, 2007), tidyverse (Wickham et al., 2019), caret, and rstatix packages.

The sensitivity of both LA systems was compared by visual assessment of the capability of distinguishing between the ablation signal and the features of gas blank, and graphical comparison of the measured counts. Additionally, NIST glass standards 610 and 612 were used for this purpose (ablation parameters are listed in Table S4). Note, signal intensities (counts) of NIST glasses are more prone to the ablation of different depths as PM samples with the majority of PM material captured in the upper layers of the filter. The ratio between the two LA systems was calculated for every element in order to i) compare ablation volumes and ii) better evaluate method sensitivity.

# 3 Results and discussion

## 3.1 LA213 parameters optimization

The LA213 system was first optimized to assure the finest possible sensitivity and repeatability. As already mentioned in the introduction part, how the laser interacts with a sample depends on sample characteristics (*e.g.* transparency, density) and laser wavelength. Usually, LA213 needs more energy (higher fluence) compared to LA193 for similar ablation. For example, NIST 600 glass series RM is optimally ablated using fluence 3–5 J cm$^{-2}$ with LA193, whereas 8–12 J cm$^{-2}$ is needed with LA213. Our samples, however, are much more complex due to their two-component structure (filter matrix and deposited PM), which does not allow to easily draw parallels with RM or other samples from the literature; instrument parameters thus have to be carefully optimized for the specific application.

In PM on a filter samples, particles are mostly deposited in top layers of the filter and are not strongly bound to filter fibres. As PM represents only a small proportion of the sample mass, impurities in the filter matrix strongly interfere with the analysis of trace PM concentrations if large amount of filter matrix is ablated. Since we are only interested in the composition of PM and not in the filter matrix itself, the optimal fluence will be strong enough to allow for the ablation of the deposited PM but low enough to ablate as little quartz fibres as possible at the same time. Therefore, relatively low fluence is preferred for the ablation of PM samples, with the correction to higher dosages (*i.e.* more overlapping shots) in case that PM still remains on the filter after the selected number of overlapping shots.

**Table 1** Optimized instrument parameters for the ablation of PM deposited on quartz fibre filters

| **Parameter** | **LA193*** | **LA213** |
|---|---|---|
| **Pre-determined parameters by educated guess** | | |
| Laser beam size | 128 µm (square mask) | 125 µm (square mask) |
| Scan speed | 256 µm $s^{-1}$ | 250 µm $s^{-1}$ |
| Acquisition time | 0.5 s | 0.5 s |
| **Optimized parameters** | | |
| Dosage | 10 | 10 |
| Repetition rate | 20 Hz | 20 Hz |
| Fluence | 1.5 J $cm^{-2}$ (with 10x demagnification) | 1.7 J $cm^{-2}$ |
| Ablated area | 3 × 12 $mm^2$ (random sampling) | 3 × 12 $mm^2$ (random sampling) |

*from Ogrizek et al. (2021)

It turned out that optimal instrument parameters are very similar for both LA systems (Table 1). In the case of LA213, 1.7 J $cm^{-2}$ was chosen as the optimal fluence, because higher fluences did not provide significant increase in the signal intensities (Fig. 1a). The observed increase in the signal intensity with increasing fluence especially in the second ablation pass can be attributed to the ablation of quartz fibre material together with its impurities at higher fluences, which should be avoided. This explanation is additionally confirmed with the lack of signal intensity increase at higher dosages (Fig. 1b). Therefore, we selected dosage 10 as sufficient for winter samples, whereas for summer samples even less dosage would be adequate.

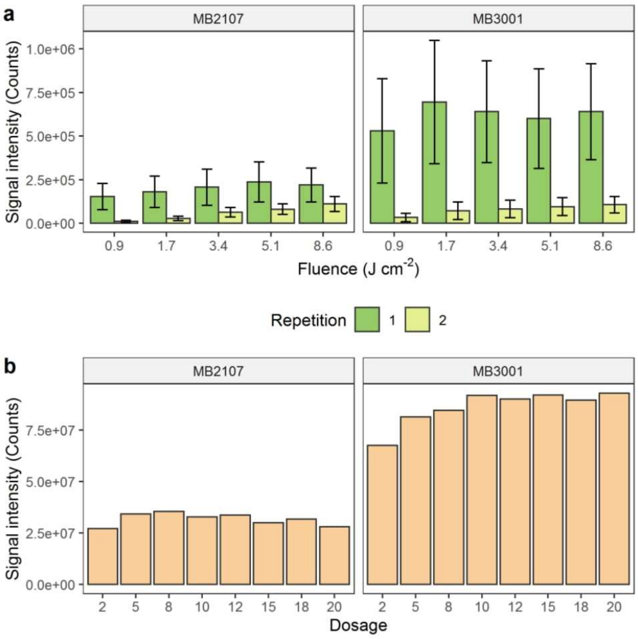

**Fig. 1** Optimization of LA213 parameters: example for Cr. One highly loaded sample (MB3001) and one sample with a low PM mass-load (MB2107) are shown. In the optimization of fluence, dosage was fixed at 10, and for the optimization of dosage, fluence 1.7 J cm$^{-2}$ was used. Error bars in A represent variability between the pixels (standard deviation). In B, the sum of pixels is shown instead of an average, not allowing us to calculate the standard deviation

We should mention at this point that instrument parameters are optimized for typical ambient PM concentration levels in Europe ($PM_{10}$ mass concentration < 50 µg m$^{-3}$). However, if samples are collected in much more polluted areas with significantly higher mass loadings, such as in Asian cities, the dosage needs to be adjusted, keeping the fluence at the determined level (*vide supra*). From this perspective, LA213 has some limitations, since the maximum repetition rate is 20 Hz, compared to LA193 where 300 Hz or even 1000 Hz can be used (Šala et al., 2020). For instance, with the maximum repetition rate of 20 Hz, scan speed has to be adjusted for dosages above 10, resulting in a prolonged measurement time.

## 3.2 Blank filter ablation

Although ablation parameters were optimized to ablate as little filter matrix as possible, in the upper layers of the filter quartz fibres and PM are intertwined together so that ablation of some fibres cannot be completely avoided. Along with the fibres, some impurities from the filter are always sampled as well. Whenever the impurities of blank filter differ significantly from the background noise (*i.e.* gas blank), their contribution needs to be accounted for during PM analysis. Therefore, filter blanks were analysed with both LA systems using the set of optimized instrument parameters and compared (Fig. 2).

The most pronounced interferences originating from blank filters that were detected with both LA systems are Al, Cr, and Mo (Fig. S1). Aluminium impurities are not problematic, since Al is one of the Earth crust elements that are naturally present in PM in relatively high concentrations even in low-polluted areas. On the other hand, Cr and Mo are less abundant in PM and in low-polluted samples non-negligible blank signals can substantially affect their determination.

Overall, with use of the optimised set of parameters, LA213 seems to ablate more blank filter material and consequently more impurities than LA193 (observe the differences between gas blanks and filter blanks in Fig. S1). With LA213, Ni was clearly detected in blank filters and some barely noticeable differences between gas and filter blanks were also found for Fe, K, Mn, Ti, and Zn. On the other hand, LA193 barely detected Ni, Sb, and Ba impurities, whereas the latter two elements were not detected with LA213 at all, indicating higher detection limits.

Among the listed elements, special attention should be paid to Cr, Ni, and Mo when using LA213 (filter blanks accounted for up to 20, 20, and 45% of low-concentration samples, respectfully), and to Cr when using LA193 (filter blank accounted for 8% of the low-concentration sample). All other impurities were low enough compared to sample concentrations to avoid an influence on the final quantification (impurities in blanks contributed <3% to the lowest sample signal in both LA systems).

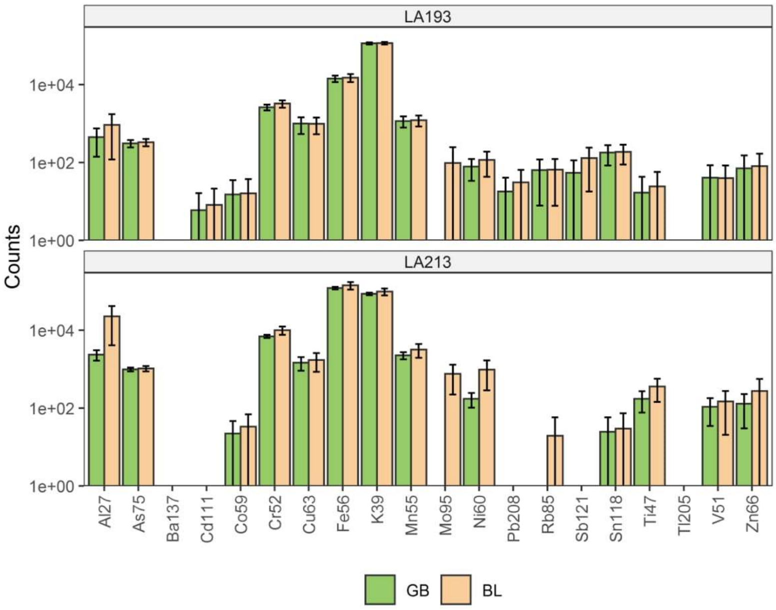

**Fig. 2** Gas blank (GB) vs. filter blank (BL): Comparison of signals from the background noise (*i.e.* GB) with the impurities in blank filters (*i.e.* BL). The plotted error bars are standard deviations between the pixels, representing their scattering

### 3.3 PM sample ablation: comparison of LA213 with LA193

It has already been explained that laser interaction with the ablated material is wavelength specific and can lead to distinctive elemental fractionation effects. The ablation of PM samples is performed in a line-scan mode and since the majority of PM mass is deposited in the upper layers of the sample, an in-depth fractionation effect is not likely to be observed. Moreover, potential fractionation effects are expected to be corrected for by calibration with matrix-matched standards. However, calibration still remains an issue in LA-ICPMS.

Since PM material on quartz fibre filter is a very specific sample in its structure, none of the commonly used RM (*e.g.* glass or gelatine standards, pressed pellets, spiked filter matrix, ...) is suitable for its calibration (Brown et al., 2013; Miliszkiewicz et al., 2015; Šala et al., 2017). Matrix-matched RM of PM on quartz fibre filter with certified elemental composition is also not yet commercially available. Although the use of ambient PM samples previously characterized with MW/ICPMS as standards for the calibration is not an ideal practice, since erroneous determination due to the MW pre-treatment step can lead to inaccurate LA-ICPMS analysis, it is a matrix-matched material and fits the purpose of our research.

The constructed calibration curves were not ideal (note that MW/ICPMS used for their standardization is not certified for all elements); but still, LOOCV analysis showed they were comparable for LA193 and LA213 (Fig. S2). Both LA systems exhibited high $R^2$, low root mean squared errors (RMSE), and low mean absolute errors (MAE) for Al, As, Co, Cu, Fe, Mn, Mo, Sb (Fig. S2). Somehow poorer performance was obtained for Cd, Rb, and Zn, with both instruments. Furthermore, we can see that LOOCV calibration curves, which are presented in Fig. S3 for the case of As, show substantial deviation from the rest of the curves only when the highest concentration measured is omitted (as part of statistical procedure). This may lead to biases in the quantification of analytes with concentrations in the upper part of each calibration curve, while confidence of the determination of low-concentration samples should not be compromised.

In Fig. S4 we compare the results of sample analyses with all three methods. Samples determined with both LA systems and MW/ICPMS do not reveal any credible evidence for the difference for any of the elements, which was also confirmed by statistical testing (Table S5). Note that MW/ICPMS results were used as calibration standards, masking eventual systemic biases due to incomplete digestion in the respective method. Airborne concentrations of all elements as determined by LA193 and LA213 are further compared in Fig. 3, Table S6, and Table S7. Higher deviations (although randomly distributed) between the LA systems are observed in the samples with the highest element concentrations, which is in line with the nature of the constructed calibration curves as explained in the previous paragraph. Moreover, the highest concentrations measured felt outside of the calibration range, which resulted in even poorer confidence of their determination. Consequently, high absolute differences between the two LA systems are observed at the highest concentrations measured. Note that according to Directive 2004/107/EC, accuracy of determination of As, Cd, and Ni in PM is reported within 40 % by MW/ICPMS. From all this we may conclude that the performance of LA213 is comparable to LA193.

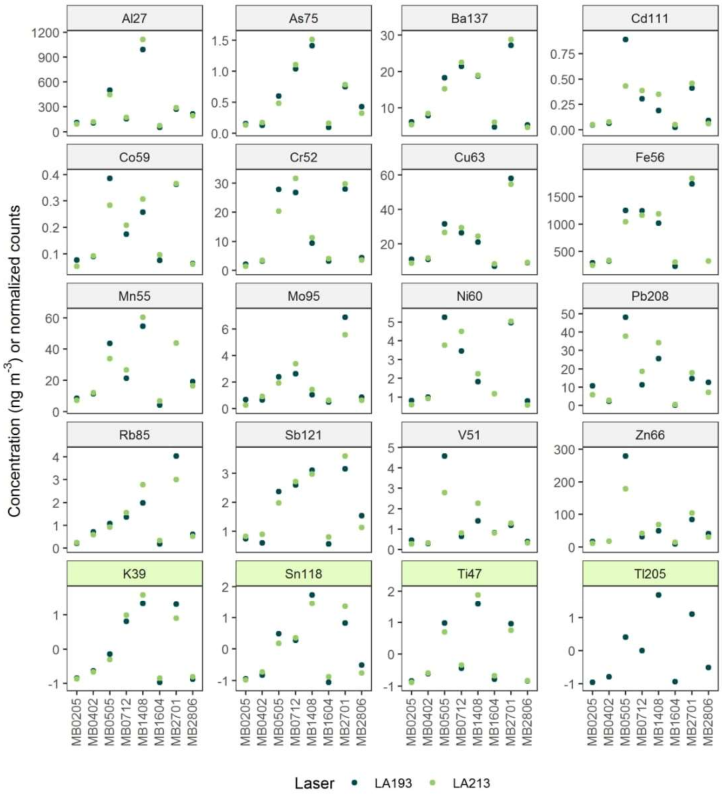

**Fig. 3** LA193 vs LA213: Comparison of ambient sample element concentrations. The top 4 rows (grey) present calibrated elements with concentration on y-axis, and the bottom row (green) are non-calibrated elements with normalized counts on y-axis, since the 4 elements (*i.e.* K, Sn, Ti, and Tl) were not measured with MW/ICPMS. Tl could only be detected with LA193

Although we showed that both LA systems perform comparably well in terms of accuracy, different sensitivity was observed for some elements. LA213 turned out to be less sensitive for Ba, Cd, Pb, Sb, Sn and Tl in PM samples (Fig. S5) as well as NIST glass standards (Fig. S6). Sb and Sn are not considered problematic, since they are usually present in PM in fairly high concentrations. On the contrast, in low-concentration samples, Ba, Cd, and Pb were at the edge of LOD in LA213 measurements, which was not the case with LA193 (refer here also to Fig. S7). We were also unable to determine Tl with LA213 in either the PM samples or NIST glass standards. Among the referenced elements in NIST 610, Tl has the lowest reported concentration (approximately 7-times lower than the other elements of interest), which points to the poor sensitivity of the method for this particular element. Besides, Tl is also volatile and could be lost during the ablation, especially with LA213. Note, however, that when particular elements are of specific interest, high LODs and/or low sensitivities can be overcome by additional optimization and introducing more material for their analysis (*e.g.* bigger beam size or longer acquisition times; the latter consequently means measuring fewer elements at a time) (van Elteren et al., 2019).

Although we observed a similar pattern in sensitivity towards different elements for real samples and NIST standards, we should not neglect the fact that with the different lasers we indeed ablated different volumes of the material due to different beam sizes (256 µm for LA193 and 125 µm for LA213), but also due to differences in the used fluence and laser wavelengths, influencing intensity of the signal (*i.e.* counts). As already mentioned, ablation volume is especially important in the case of NIST standards. Therefore, in order to understand differences between both ablations, we further examined the ratios between the elements measured with the LA systems in both RM, which are shown in Table S8.

Based on the ratios of most elements (*i.e.* Al, As, Co, Cr, Cu, Fe, K, Mn, Ni, Ti, V, and Zn), larger volumes seem to be ablated with LA213 compared to LA193. If this is true, LA213 indeed exhibits much lower sensitivity for the above-mentioned elements. Furthermore, when comparing the ratios for NIST 610 and 612, more abnormalities were found in the case of NIST 612 (see Table S8), which implies more fractionation effects in the case of NIST 612. Similar observations were reported by Guillong et al. (2003), where fractionation indexes of LA193 and LA213 were different in the case of NIST 612, but still very similar in the case of NIST 610.

Ba, Cd, Pb, Sb, Sn, and Tl are normally produced by anthropogenic activities (*e.g.* traffic, industry) and usually exhibit lower airborne concentrations than elements originating from natural sources (*e.g.* Al, Fe, K). In source apportionment studies, those 6 elements are usually associated with traffic or traffic-related emission factors as are break and tyre wear (*e.g.* Ba, Cd, Pb, Sb, Sn), biomass burning (*e.g.* Cd, Tl), or industrial emission factors as are metallurgical emissions (*e.g.* Pb, Tl) (Almeida et al., 2020; Belis et al., 2013; Ferreira et al., 2016; Landis et al., 2017; Massimi et al., 2020). Our samples were collected in an urban environment, close to a road with heavy traffic where anthropogenic emissions are relatively constant regardless of the seasons. Nevertheless, with LA213 we could barely detect some of these elements in summer samples, which may be generally problematic when studying samples collected in warmer parts of the year or in rural areas with less traffic and industrial emission sources. From this perspective, LA193 is a preferential choice of use in source apportionment studies conducted in low-polluted areas or where Tl is the targeted element of interest (*e.g.* determination of the influence of specific industry on air pollution), unless LA213 method parameters are further optimized for these elements (Karbowska, 2016).

Even though the sensitivity of LA213 is poorer than of LA193 for some elements, it is still sufficient to meet the current legislation (limit values are 6, 5, 20, and 500 ng $m^{-3}$ for As, Cd, Ni, and Pb, respectfully; EU Directive 2004/107/EC and 2008/50/EC), and to compete with the current standard method (low limit of working range is set at 0.5, 0.1, 2, and 1 ng $m^{-3}$ for As, Cd, Ni, and Pb, respectfully). In our work, airborne concentrations were in the range of 0.09–1.5 ng $m^{-3}$ for As, 0.02–0.9 ng $m^{-3}$ for Cd, 0.6–5.3 ng $m^{-3}$ for Ni, and 0.3–50 ng $m^{-3}$ for Pb as shown in Fig. 3; we were able to determine them all, although some concentrations fall below the certified LOD of MW/ICPMS. Multi-element determination and other pros of the method can be exploited as comparable with MW/ICPMS, without concerning about the problems connected with MW digestion in the case of LA-ICPMS. Therefore, we can conclude that LA213 performs suitably well for monitoring of elemental concentrations in PM according to the current legislation and is a valid alternative to the more expensive LA193 system.

## 4 Conclusions and outlook

Striving for sustainability has become an important part of our everyday life. Analytical techniques often produce large quantity of toxic chemical waste and to achieve sustainable future, green analytical methods have to be promoted even in research laboratories. Air quality monitoring is one of the continuous processes where green analytical methods are especially appreciated. The intention of detecting pollution for the purpose of its mitigation and at the same time producing toxic waste and polluting the environment seems somehow contradictory. Moreover, monitoring network is expected to continuously grow and extend even to the less developed countries, which will multiply the number of analyses and consequently their effect on the environment. Green analytical methods with a minimal burden to the environment should thus replace the old methods, whenever possible.

One such example is the proposed LA-ICPMS for the elemental characterization of PM instead of the standardized MW/ICPMS method. Many different LA systems are currently available on the market, varying in performance and price availability. We show that the 193 nm excimer LA system enables low-limit determination of all 20 elements of interest and is presented as a preferable choice in source apportionment studies, where multi-element quantification is especially appreciated. On the other hand, 213 nm solid state LA system exhibits slightly higher LODs for some elements, which can be critical in low-polluted samples. Nevertheless, LA213 is still shown satisfactory for use in the elemental determination of PM according to the current legislation and it can be further fine-tuned for specific target analytes or extremely low-concentration samples. Therefore, we assess the cheaper LA213 system adequate for air-quality monitoring purposes, which lowers the initial investment needed for the transition to the greener analytical alternative.

Just as standard MW/ICPMS has many drawbacks (*e.g.* incomplete digestion, limited RM), LA-ICPMS also has some limitations. But it is continuously improving and actively developing in the direction of having more and more commercially available certified matrix matched standards for various calibration purposes, and autosamplers customized for specific samples. This is necessary for assuring the required traceability in regulatory agencies and facilitating the analysis of large number of samples. We believe LA-ICPMS is the green analytical method on the rise, that can contribute with a small step towards achieving the desired sustainable future even within air-quality monitoring.

## Declarations

**Ethics approval and consent to participate** Not applicable. No human or animal subject were involved in the study.

**Consent for publication** Not applicable.

**Availability of data and material** The datasets generated during and/or analysed during the current study are available from corresponding author on reasonable request.

**Competing interests** The authors have no relevant financial or non-financial interests to disclose.

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**Author Contributions** Monika Ogrizek: Investigation, Formal analysis, Writing – Original Draft, Visualization. Ana Kroflič: Conceptualization, Writing – Review & Editing, Supervision, Funding acquisition. Markéta Holá: Investigation, Writing – Review & Editing. Tomáš Vaculovič: Investigation, Writing – Review & Editing. Martin Šala: Conceptualization, Methodology, Writing – Original Draft, Supervision, Funding acquisition.

## References

Aldabe, J., Santamaria, C., Elustondo, D., Lasheras, E., Santamaria, J.M., 2013. Application of microwave digestion and ICP-MS to simultaneous analysis of major and trace elements in aerosol samples collected on quartz filters. Anal. Methods 5(2), 554-559.

Almeida, S.M., Manousakas, M., Diapouli, E., Kertesz, Z., Samek, L., Hristova, E., Šega, K., Alvarez, R.P., Belis, C.A., Eleftheriadis, K., Albania, Civici, N., Radic, R., Vukic, L., Hristova, E., Veleva, B., Šega, K., Bešlic, I., Davila, S., Godec, R., Manousakas, M., Diapouli, E., Vratolis, S., Eleftheriadis, K., Kertesz, Z., Belis, C.A., Bernatonis, M., Djukanovic, G., Jancic, D., Samek, L., Furman, L., Stegowski, Z., Almeida, S.M., Galinha, C., Balan, V., Nikolovska, L., Stefanovska, A., Radenkovic, M., Kneževic, J., Banu Oztas, N., Cantay, E., Turchenko, D.V., Abdullaev, S., Padilla Alvarez, R., Karydas, A.G., The, I.E.R.S.G., 2020. Ambient particulate matter source apportionment using receptor modelling in European and Central Asia urban areas. Environ. Pollut. 266.

Bai, H.M., Yan, R.S., Gao, W.K., Wei, J., Seong, M., 2022. Spatial representativeness of PM2.5 monitoring stations and its implication for health assessment. Air Qual. Atmos. Health 15(9), 1571-1581.

Belis, C.A., Karagulian, F., Larsen, B.R., Hopke, P.K., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos. Environ. 69, 94-108.

Brown, R.J.C., Jarvis, K.E., Disch, B.A., Goddard, S.L., 2013. An investigation of calibration materials for the measurement of metals in ambient particulate matter on filters by LA-ICP-MS. Int. J. Environ. Anal. Chem. 93(3), 335-348.

Chatoutsidou, S.E., Kopanakis, I., Lagouvardos, K., Mihalopoulos, N., Torseth, K., Lazaridis, M., 2019. PM10 levels at urban, suburban, and background locations in the eastern Mediterranean: local versus regional sources with emphasis on African dust. Air Qual. Atmos. Health 12(11), 1359-1371.

Ferreira, A.J.D., Soares, D., Serrano, L.M.V., Walsh, R.P.D., Dias-Ferreira, C., Ferreira, C.S.S., 2016. Roads as sources of heavy metals in urban areas. The Covões catchment experiment, Coimbra, Portugal. Journal of Soils and Sediments 16(11), 2622-2639.

Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier van der Gon, H., Facchini, M.C., Fowler, D., Koren, I., Langford, B., Lohmann, U., Nemitz, E., Pandis, S., Riipinen, I., Rudich, Y., Schaap, M., Slowik, J.G., Spracklen, D.V., Vignati, E., Wild, M., Williams, M., Gilardoni, S., 2015. Particulate matter, air quality and climate: lessons learned and future needs. Atmos. Chem. Phys. 15(14), 8217-8299.

Gerboles, M., Buzica, D., 2008. Intercomparison exercise for heavy metals in PM10, EUR 23219 EN. Office for Official Publications of the European Communities, Luxembourg.

Gilbert, S.E., Danyushevsky, L.V., Goemann, K., Death, D., 2014. Fractionation of sulphur relative to iron during laser ablation-ICP-MS analyses of sulphide minerals: implications for quantification. J. Anal. At. Spectrom. 29(6), 1024-1033.

Gini, M., Manousakas, M.-I., Kantarelou, V., Karydas, A.-G., Chiari, M., Migliori, A., Civici, N., Veleva, B., Šega, K., Samek, L., Samara, C., Kertesz, Z., Osan, J., Eleftheriadis, K., 2021. Inter-laboratory comparison of ED-XRF/PIXE analytical techniques in the elemental analysis of filter-deposited multi-elemental certified reference materials representative of ambient particulate matter. Science of The Total Environment 780, 146449.

Goix, S., Uzu, G., Oliva, P., Barraza, F., Calas, A., Castet, S., Point, D., Masbou, J., Duprey, J.L., Huayta, C., Chincheros, J., Gardon, J., 2016. Metal concentration and bioaccessibility in different particle sizes of dust and aerosols to refine metal exposure assessment. J. Hazard. Mater. 317, 552-562.

Gonzalez, J., Mao, X.L., Roy, J., Mao, S.S., Russo, R.E., 2002. Comparison of 193, 213 and 266 nm laser ablation ICP-MS. J. Anal. At. Spectrom. 17(9), 1108-1113.

Guillong, M., Gunther, D., 2002. Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry. J. Anal. At. Spectrom. 17(8), 831-837.

Guillong, M., Horn, I., Gunther, D., 2003. A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd : YAG laser for laser ablation ICP-MS. J. Anal. At. Spectrom. 18(10), 1224-1230.

Hu, X., Zhang, Y., Ding, Z.H., Wang, T.J., Lian, H.Z., Sun, Y.Y., Wu, J.C., 2012. Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China. Atmos. Environ. 57, 146-152.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N., 2014. Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary Toxicology 7(2), 60-72.

Jochum, K.P., Stoll, B., Weis, U., Jacob, D.E., Mertz-Kraus, R., Andreae, M.O., 2014. Non-Matrix-Matched Calibration for the Multi-Element Analysis of Geological and Environmental Samples Using 200 nm Femtosecond LA-ICP-MS: A Comparison with Nanosecond Lasers. Geostand. Geoanal. Res. 38(3), 265-292.

Karagulian, F., Belis, C.A., Dora, C.F.C., Prüss-Ustün, A.M., Bonjour, S., Adair-Rohani, H., Amann, M., 2015. Contributions to cities' ambient particulate matter (PM): A systematic review of local source contributions at global level. Atmos. Environ. 120, 475-483.

Karbowska, B., 2016. Presence of thallium in the environment: sources of contaminations, distribution and monitoring methods. Environmental Monitoring and Assessment 188(11), 640.

Landis, M.S., Pancras, J.P., Graney, J.R., White, E.M., Edgerton, E.S., Legge, A., Percy, K.E., 2017. Source apportionment of ambient fine and coarse particulate matter at the Fort McKay community site, in the Athabasca Oil Sands Region, Alberta, Canada. Science of The Total Environment 584-585, 105-117.

Lelieveld, J., Evans, J.S., Fnais, M., Giannadaki, D., Pozzer, A., 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature 525(7569), 367-371.

Luo, T., Wang, Y., Li, M., Zhang, W., Chen, H.H., Hu, Z.C., 2020. Determination of Major and Trace Elements in Alloy Steels by Nanosecond and Femtosecond Laser Ablation ICP-MS with Non-matrix-matched Calibration. Atom. Spectrosc. 41(1), 11-19.

Massimi, L., Ristorini, M., Astolfi, M.L., Perrino, C., Canepari, S., 2020. High resolution spatial mapping of element concentrations in PM10: A powerful tool for localization of emission sources. Atmos. Res. 244, 11.

Miliszkiewicz, N., Walas, S., Tobiasz, A., 2015. Current approaches to calibration of LA-ICP-MS analysis. J. Anal. At. Spectrom. 30(2), 327-338.

Ogrizek, M., Jaćimović, R., Šala, M., Kroflič, A., 2021. No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters. Talanta 226, 122110.

Ogrizek, M., Kroflič, A., Šala, M., 2022. Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter. Trends in Environmental Analytical Chemistry 33, e00155.

Pant, P., Lal, R.M., Guttikunda, S.K., Russell, A.G., Nagpure, A.S., Ramaswami, A., Peltier, R.E., 2019. Monitoring particulate matter in India: recent trends and future outlook. Air Qual. Atmos. Health 12(1), 45-58.

Rovelli, S., Nischkauer, W., Cavallo, D.M., Limbeck, A., 2018. Multi-element analysis of size-segregated fine and ultrafine particulate via Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. Anal. Chim. Acta 1043, 11-19.

Roy, R., Jan, R., Yadav, S., Vasave, M.H., Satsangi, P.G., 2016. Study of metals in radical-mediated toxicity of particulate matter in indoor environments of Pune, India. Air Qual. Atmos. Health 9(6), 669-680.

Swami, K., Judd, C.D., Orsini, J., Yang, K.X., Husain, L., 2001. Microwave assisted digestion of atmospheric aerosol samples followed by inductively coupled plasma mass spectrometry determination of trace elements. Fresenius J. Anal. Chem. 369(1), 63-70.

Šala, M., Šelih, V.S., Stremtan, C.C., van Elteren, J.T., 2020. Analytical performance of a high-repetition rate laser head (500 Hz) for HR LA-ICP-QMS imaging. J. Anal. At. Spectrom. 35(9), 1827-1831.

Šala, M., Šelih, V.S., van Elteren, J.T., 2017. Gelatin gels as multi-element calibration standards in LA-ICP-MS bioimaging: fabrication of homogeneous standards and microhomogeneity testing. Analyst 142(18), 3356-3359.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy Metal Toxicity and the Environment, in: Luch, A. (Ed.) Molecular, Clinical and Environmental Toxicology: Volume 3: Environmental Toxicology. Springer Basel, Basel, pp. 133-164.

Trippetta, S., Sabia, S., Caggiano, R., 2016. Fine aerosol particles (PM1): natural and anthropogenic contributions and health risk assessment. Air Qual. Atmos. Health 9(6), 621-629.

Tsiouri, V., Kakosimos, K.E., Kumar, P., 2015. Concentrations, sources and exposure risks associated with particulate matter in the Middle East Area-a review. Air Qual. Atmos. Health 8(1), 67-80.

van Elteren, J.T., Šelih, V.S., Šala, M., 2019. Insights into the selection of 2D LA-ICP-MS (multi)elemental mapping conditions. J. Anal. At. Spectrom. 34(9), 1919-1931.

Wang, C.F., Jeng, S.L., Lin, C.C., Chiang, P.C., 1998. Preparation of airborne particulate standards on PTFE-membrane filter for laser ablation inductively coupled plasma mass spectrometry. Anal. Chim. Acta 368(1-2), 11-19.

Wickham, H., 2007. Reshaping Data with the reshape Package. Journal of Statistical Software 21(12), 1 - 20.

Wickham, H., Averick, M., Bryan, J., Chang, W., D'Agostino McGowan, L., François, R., Grolemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T.L., Miller, E., Bache, S.M., Müller, K., Ooms, J., Robinson, D., Seidel, D.P., Spinu, V., Takahashi, K., Vaughan, D., Wilke, C., Woo, K., Yutani, H., 2019. Welcome to the tidyverse. Jurnal of Open Source Software 4(43), 1686.

Wohlgemuth-Ueberwasser, C.C., Jochumb, K.P., 2015. Capability of fs-LA-ICP-MS for sulfide analysis in comparison to ns-LA-ICP-MS: reduction of laser induced matrix effects? J. Anal. At. Spectrom. 30(12), 2469-2480.

Zhang, T.F., Mao, W.H., Gao, J.H., Song, X.Q., Li, L.F., Sun, X.B., Ding, X.F., Li, J.B., Zhai, Y.K., Ma, W., Zhao, J., 2022. The effects of PM2.5 on lung cancer-related mortality in different regions and races: A systematic review and meta-analysis of cohort studies. Air Qual. Atmos. Health 15(9), 1523-1532.

## 3.4 Article 4: Characterization of Fresh PM Deposits on Calcareous Stone Surfaces: Seasonality, Source Apportionment and Soiling Potential

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One of the negative effects of PM is the deposition on cultural heritage, as soiling is mostly a reason for surface blackening, but can also cause corrosion followed by material degradation and loss, which is clearly seen on many historic buildings, churches, and calcareous outdoor sculptures. The level of the impact on stone surfaces depends on the composition of ambient PM, which is defined by its sources. However, the correlation between ambient air pollution and PM deposits is still underinvestigated.

In the following article, fresh PM deposits on calcareous stone surfaces were investigated and correlated with ambient PM pollution. Two types of calcareous stones (*i.e.* marble and limestone) were exposed to ambient air in sheltered and unsheltered positions for approximately one month on a rooftop of the National Institute of Chemistry in Ljubljana. At the same time, one blank sample for every stone type was stored in a laboratory to avoid contamination with ambient PM. In parallel with stone exposure, ambient PM was sampled by a CASS system, scanning mobility particle sizer (SMPS), and PM sampler, for the investigation of ambient PM composition and source apportionment. The measuring campaign was repeated in every season to include seasonal variation of PM sources and climatic conditions. Ambient PM was characterized on-line for carbonaceous aerosol by the CASS system, diurnal variation of particle number and size distributions was studied by SMPS, PM mass was determined off-line by gravimetry, and elemental and ionic composition were measured by LA-ICPMS and IC. The results of PM composition were further applied for the identification of sources using two different models: carbonaceous aerosol apportionment and PMF analysis. The stone samples were surface-characterized by reflectance measurements, scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDXS), and surface elemental composition was also determined by LA-ICPMS. Elemental composition determined by LA-ICPMS and SEM-EDXS was correlated with the elemental composition of $PM_{2.5}$ samples in the corresponding season.

Carbonaceous aerosols were differentiated in six different aerosol types according to their absorbance and sources: traffic and biomass burning-associated black carbon, primary organic aerosol with absorbing and non-absorbing properties, and secondary organic aerosols with absorbing and non-absorbing properties. The model revealed typical seasonal variation with a large contribution of biomass burning emissions in winter, while SOA formation dominated in summer. Traffic emissions were relatively constant throughout the year, with roughly 20 % contribution to the carbonaceous aerosols. Additional PM sources contributing to the total $PM_{2.5}$ mass investigated were explained using the PMF model, where six major factors were identified: nitrate, biomass burning, crustal dust, marine SOA, sulphate, traffic, and a minor unexplained contribution. The predominant source of $PM_{2.5}$ in Ljubljana turned out to be traffic with 30 % contribution to the PM mass. Seasonal variation was explained by winter biomass burning for heating purposes (nitrate and biomass burning factors) and enhanced photochemistry in summer enabling SOA production (sulphate factor). The crustal dust factor was especially pronounced in some special events of Saharan dust advection into the region (long-range transport), which was identified by the specific enrichment of crustal elements (*e.g.* Al, As, Ba, Co, Cr, Fe, Mn, Rb, and V).

When comparing elemental composition of ambient PM and stone deposits, seasonal trends and other variations (*i.e.* specific Saharan dust events) generally agreed for most elements, except for some divergences (*e.g.* Mg, Mn, and Na in autumn), probably due to different particle sizes collected on stone surfaces (*i.e.* TSP) and on $PM_{2.5}$ filter samples.

This article was published under the project *Impacts of PM pollution to cultural heritage* and the candidate importantly contributed to it with i) the determination of elemental composition of ambient PM by the LA-ICPMS method previously developed, ii) LA-ICPMS data processing (including stone samples), and iii) statistical evaluation of the elemental composition of PM samples and stone deposits, and ionic composition of PM samples. The statistical evaluation was performed in program R using Shapiro-Wilk and Levene's tests to check the conditions of normality and equality of variance, Mann-Whitney test for comparison of exposed with blank stone and sheltered with unsheltered position, and Kruskal-Wallis test for investigating seasonal trends, where the Benjamini & Hochberg p-value correction was used in all multiple testing procedures. The candidate was also involved in field campaigns and helped with stone surface analysis and manuscript writing.

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# Characterization of fresh PM deposits on calcareous stone surfaces: Seasonality, source apportionment and soiling potential

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## HIGHLIGHTS

- Interaction between heritage materials and airborne particles is poorly understood.
- Fresh deposits are characterized to be able to study aging after the deposition.
- PM source apportionment is correlated with surface reflectance and chemistry.
- Surface deposits resemble main PM sources but do not sum up on long time-scales.
- Light absorption by black carbon causing soiling still exceeds that of brown carbon.

## GRAPHICAL ABSTRACT

## ARTICLE INFO

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Surface darkening
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Elemental analysis
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## ABSTRACT

Particulate matter (PM) pollution is one of the major threats to cultural heritage outdoors. It has been recently implied that organic aerosols will prevail over inorganic carbon particulates in the future, changing the main mechanisms of damage caused by poor air quality to calcareous heritage in particular. We studied fresh particulate deposits on marble and limestone surfaces exposed to urban air in sheltered and unsheltered configurations. Due to different air pollution sources in different seasons, the amount and composition of surface deposits varied throughout the year. The main and most constant contributor to $PM_{2.5}$ (particles smaller than 2.5 μm) were primary traffic emissions (30 %), followed by secondary formation of acidic inorganic aerosols, such as sulphate in summer and nitrate in winter (33 % altogether), and seasonal biomass-burning emissions (14 %). Although biomass burning is the major source of primary organic aerosols including the light-absorbing fraction that prevailed over black carbon (BC) in colder months (up to 60 % carbonaceous aerosol mass), we show that surface darkening causing the soiling effect is still governed by the minor BC fraction of atmospheric aerosols, which remained below 20 % of the carbonaceous aerosol mass throughout the year. This, however, can change in remote environments affected by biomass-burning emissions, such as winter resorts, or by rigorous BC mitigation measures in the future. In the short run, sheltered positions were less affected

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by different removal processes, but we show that surface deposits are not simply additive when considering longer periods of time. This must be taken into account when extrapolating surface accumulation to longer time scales.

## 1. Introduction

Outdoor materials are permanently exposed to weathering in combination with air pollution. Their interactions with airborne pollutants lead to material degradation (atmospheric corrosion) and loss, including deterioration of cultural heritage objects causing immeasurable damage to the community (Tidblad et al., 2012). Surface blackening due to particulate matter (PM) deposition (soiling) is another major hazard to heritage materials (Lombardo et al., 2010), requiring periodical cleaning and often resulting in unwanted damage especially to stone objects (Brimblecombe and Grossi, 2005).

In the past century, $SO_2$ was by far the most important factor influencing calcareous stone recession outdoors (Giavarini et al., 2008). Until now, $SO_2$ emissions have been successfully mitigated and the situation has changed from $SO_2$-dominant to a multipollutant one (Vidović et al., 2022). Recently, comparable contributions of dry $HNO_3$ deposition (closely connected with $NO_x$ emissions and $O_3$ in combination with moisture), $SO_2$ deposition, acidic precipitation (due to dissolved $CO_2$ (Karst effect) and anthropogenic $H_2SO_4$ and $HNO_3$ acids in acid rain), and PM deposition to limestone deterioration have been estimated in urban areas (Bonazza et al., 2009; De Marco et al., 2017). However, according to Di Turo et al. (2016), increased PM concentrations were responsible for the estimated positive trend in limestone corrosion levels between years 2000 and 2010 in Europe, which warrants attention.

Airborne PM, which affects stone surfaces with both soiling and surface corrosion, is typically composed of inorganic ions, trace metals, and carbonaceous aerosol (CA), which includes two fractions: black carbon (BC or elemental carbon) and organic aerosol (OA) that can be further divided into the light-absorbing OA or brown carbon (BrC) and non-absorbing OA ($OA_{non\text{-}abs}$). Carbon content in CA and OA is often expressed as total carbon (TC) and organic carbon (OC), respectively. The composition of PM is closely linked to its emission sources, thus exhibiting strong seasonality. For instance, BC originates from various combustion sources (vehicle emissions, residential coal and biomass burning emissions), contributing at varying amounts to the level of BC pollution throughout the year, while biomass burning specifically is recognized as the major source of BrC on a global scale (Laskin et al., 2015), which is consequently predominant in colder months due to wide use of fireplaces and wood burning for heating. On the other hand, $OA_{non\text{-}abs}$ is largely connected with biogenic emissions and predominates in remote regions and in the warmer part of a year (Martinsson et al., 2020).

The reactive OA fraction has been found to predominate over the more inert BC in black crusts of historic buildings at many sites in Italy, which contradicts the general belief that BC is responsible for damage caused to calcareous historic objects (Bonazza et al., 2005). Already back in 1993, Saiz-Jimenez (1993) studied deposition of airborne organics on historic buildings and concluded that composition of each crust is governed by the composition of the air in the area. In support, Bonazza et al. (2005) showed that historic damage layers are a record of environmental changes over time, with their chemical composition reflecting atmospheric pollution due to combustion sources, and concluded that soiling due to OA will likely prevail in the next future. Akos et al. (2011) further compared the content of polyaromatic hydrocarbons (PAH) in ambient PM and in the crusts of historic buildings, and recognized the important role of dust in accumulating PAHs. Moreover, Ozga et al. (2014) concluded that damage layer composition reflects air pollution in the surrounding area; however, Fermo et al. (2018) did not find any direct correlation between atmospheric gaseous precursors and the related ions in investigated PM deposits.

While the exact role of atmospheric PM in stone degradation remains elusive (Fermo et al., 2015), it is clear that surface deposits can contain atmospheric particles from both natural and anthropogenic sources (Calparsoro et al., 2017). Although BC is unequivocally recognized as the major contributor to surface soiling, very little to nothing is known about the influence of the increasing BrC fraction in atmospheric aerosols and how unique physicochemical characteristics of ambient PM from different sources in different seasons affect particulate deposition and stone surface degradation beyond the damaging potential of contained inorganic acids.

In this work, we analyse fresh seasonal PM deposits on calcareous (limestone and marble) stones representing the majority of cultural heritage objects, in order to later compare them with aged stone surfaces. We first physico-chemically characterize atmospheric PM in Ljubljana, Slovenia in order to correlate surface properties of exposed carbonaceous stones with different PM pollution conditions in different seasons. During one-month outdoor exposures of stones under sheltered and unsheltered conditions, ambient $PM_{2.5}$ samples (*i.e.* airborne particulates smaller than 2.5 μm) were collected and analysed for ionic and elemental composition. In parallel, PM size distribution, TC concentration and optical properties were measured and used to apportion carbonaceous aerosols to their sources (traffic, biomass burning; primary, secondary aerosols) and particular light-absorbing fractions (BC, BrC, $OA_{non\text{-}abs}$). Positive matrix factorization (PMF) analysis was further applied to identify the main sources of PM pollution at the site of exposure, which differ with different seasons. Specific methodology was set up for stone surface characterization after each exposure; stones were investigated for their surface morphology, reflectance (as a measure of soiling), and elemental composition, which is finally correlated with airborne $PM_{2.5}$ measurements.

## 2. Experimental section

### 2.1. Location and experimental design

Surface-polished limestone and marble samples (5 × 5 × 1.5 cm; Fig. 1a) were exposed to outdoor weathering and urban pollution on the

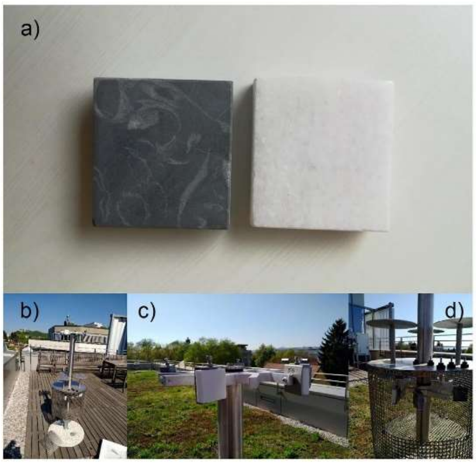


**Fig. 1.** a) Limestone (grey) and marble (white) stone that were exposed on b) a custom-made carousel for air pollution exposure studies with c) unsheltered and d) sheltered positions for stone samples.

terrace of the National Institute of Chemistry in Ljubljana, Slovenia. The stones were vertically mounted on a custom-made carousel, in sheltered and unsheltered positions (Fig. 1b-d). One-month seasonal exposures were performed from July 2020 to July 2021. One limestone and one marble stone were exposed in every position in each season (autumn: 3.11.–4.12.2020; winter: 19.1.–17.2.2021; spring: 14.5.–18.6.2021; summer: 26.6.–26.7.2021), while one set of stones (2 + 2) was periodically exposed in all four consecutive seasonal campaigns (*i.e.* 14.7.–19.8.2020, 3.11.–4.12.2020, 19.1.–17.2.2021, 14.5.–18.6.2021). After each exposure, stones were analysed for surface reflection and stored in a freezer until further analyses. During the project, one stone of each type was stored in a laboratory and used as a blank sample for chemical analyses.

In parallel, air quality monitoring with an emphasis on atmospheric PM was conducted with dedicated online instrumentation and sampling for offline analyses. At the end, two-weeks data was analysed for every campaign; the list of samples and corresponding meteorological conditions are collected in the Supporting information, Table S1.

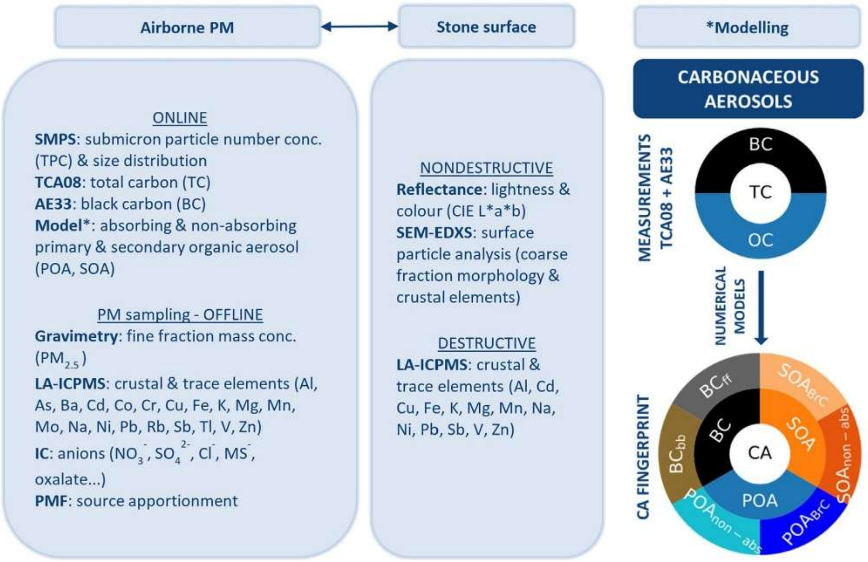
### 2.2. Materials and methods

Performed analyses and selected measurement parameters are schematically presented in Scheme 1.

During the campaigns, particle number concentration and number size distribution were measured in real time using a Scanning Mobility Particle Sizer (SMPS Spectrometer 3936L75, TSI). Measurements of TC and BC were performed with a Carbonaceous Aerosol Speciation System (CASS, Magee Scientific), which is a combined unit of a TCA08 Total Carbon Analyzer (Rigler et al., 2020) and the Aethalometer® AE33 (Drinovec et al., 2015). TCA08 measures the concentration of TC by a rapid combustion of PM collected on a quartz filter at 940 °C and was operated at 1-h time intervals, sampling $PM_{2.5}$ fraction at $16.7\,L\,min^{-1}$. The tandem Aethalometer AE33 measures aerosol light absorption at seven wavelengths (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm and 950 nm) and reports equivalent BC concentration at 880 nm by applying a specific mass absorption cross-section ($7.77\ m^2\,g^{-1}$). Again, a size-selective inlet was used to sample $PM_{2.5}$ at a flow rate of $5\ L\,min^{-1}$. High time-resolution data (1 min resolution) was then averaged to 1 h, to synchronize with the TC measurements. AE33 uses a "dual-spot" methodology to correct for the filter loading effect in real-time (Drinovec et al., 2015). The multiple scattering in the filter matrix was corrected by a correction factor C of 1.39. The difference between TC and BC corresponds to the OC fraction (Rigler et al., 2020). Online BC, TC and OC concentrations were later validated by comparison with offline analysis of PM samples (Fig. S1).

Atmospheric PM samples were simultaneously collected on quartz fibre filters (Pall Tissuquartz™ 2500 QAT-UP, Φ47 mm) using a low-volume PM sampler (Giano, Dado lab) with a $PM_{2.5}$ impactor head. Air flowrate was $2.3\ m^3\,h^{-1}$ and after 24 h sampling, filters were stored in a cooled compartment inside the sampler. The filters were conditioned in a thermostated room for at least 24 h prior to weighing before and after sampling (22 ± 1 °C, 50 ± 5 % RH), and average daily $PM_{2.5}$ concentrations in the air were calculated. However, quartz fibre filters are very fragile and quite some masses obtained were negative. Therefore, $PM_{2.5}$ concentrations as obtained from the nearest air quality monitoring station of the Slovenian Environment Agency (ARSO, approx. 5 air km distance) are considered in this work (Table S1). When available, our $PM_{2.5}$ concentrations correlated well with the data obtained from ARSO (Fig. S2). Every filter was cut in pieces needed for particular analysis and kept in a freezer.

As is typical for ion analysis, the anions were determined and quantified with ion chromatography. One $cm^2$ filter was extracted in 1 mL MilliQ water (18.2 mΩ cm at 25 °C, <3 ppb TOC) on an orbital shaker at 300 rpm for 30 min. MilliQ water was daily collected fresh from a Millipore purification system (Bedford, MA, USA). Extracts were filtered (RC, 0.20 μm) and analysed with a Dionex ICS 3000 chromatograph equipped with an eluent generator and a conductivity detector. A precolumn (Dionex IonPac AG11-HC, 4 × 50 mm) and an analytical column (Dionex IonPac AS11-HC, 4 × 250 mm) were used to achieve desired analyte separation. More details about the analysis are given in Kušan et al. (2020). The following anions were successfully quantified in the samples: fluoride, lactate,



**Scheme 1.** Schematic representation of the experimental design including the flow chart of eight steps modelling procedure to apportion carbonaceous aerosol into six components.

methanesulfonate (MS), chloride, nitrite, nitrate, sulphate, oxalate, and phosphate. Their measured airborne concentrations can be found in Table S2. Although cations are also typically measured by ion chromatography, Na, K, Ca and Mg were rather determined together with other trace elements by laser ablation inductively-coupled plasma mass spectrometer (LA-ICPMS, see below).

Elemental composition of collected PM was determined directly from a solid sample by a nanosecond excimer laser ablation (LA) system (193 nm ArF*; Analyte G2, Teledyne Photon Machines Inc., Bozeman, MT) interfaced with a quadrupole inductively-coupled plasma mass spectrometer (ICPMS; Agilent 7900 ×, Agilent Technologies, Santa Clara CA). The method is described in detail elsewhere (Ogrizek et al., 2021) and it has been shown to be competitive with other elemental analysis techniques in the case of PM (Ogrizek et al., 2022) as well as heritage materials (Giussani et al., 2009). Briefly, the filter samples were cut and simply mounted on a microscopic glass and inserted into a holder for analysis. The ablation was performed in a HelEx II two-volume ablation cell with helium as a carrier gas (cup flow 0.5 L $\min^{-1}$ and cell flow 0.3 L $\min^{-1}$) and argon as a makeup gas (0.8 L $\min^{-1}$). NIST glass SRM 612 was measured before and after every sample to observe potential instrument drift during the several-hour measurement. Instrument operation parameters are shown in Table S3. Every time, 3 × 12 $mm^2$ of a PM loaded filter was ablated, which has been shown representative of the whole filter (Ogrizek et al., 2021). Calibration was performed by measuring matrix-matched standards under the same operation conditions on the same day. Since a suitable matrix-matched reference material is not commercially available, $PM_{10}$ samples collected on quartz fibre filters in different seasons in Maribor, Slovenia, for which elemental concentrations had already been determined with a standard method by microwave digestion and ICPMS according to EN14902, were used for calibration purpose. Twenty elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Tl, V, and Zn) were measured simultaneously and the corresponding airborne concentrations are given in Table S4.

At the end of every campaign, stones were analysed for their surface deposits and reflectance. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (SEM-EDXS) were carried out using an FE-SEM Zeiss Supra TM 35 VP (Carl Zeiss, Oberkochen, Germany) field emission scanning electron microscope equipped with an energy-dispersive X-ray (EDX) spectrometer SDD EDX Ultim Max 100 (Oxford Instru-ments, Oxford, UK). The operating voltage was set to 1 kV for SEM and 20 kV for EDXS. Reflectance of the samples were measured using an i1-Pro spectrometer (X-Rite) in the visible spectral range (380–730 nm in 10-nm steps) with 45°/0° ring illumination optics (DIN 5033). The diameter of the measurement aperture is 4.5 mm. Each measurement was performed on 3 identical-location sampling positions and average values are reported for every sample.

Elemental composition of the deposits was studied with the same LA-ICPMS system as used for the PM samples, with use of similar instrumental parameters. The only difference was the lower fluence used in this case (0.43 J $cm^{-2}$), because the goal was to ablate only the deposited PM material without the stone itself. Note that a high background signal from the stone could hinder the analysis or even cover up the signal of trace elements present in the deposited PM. Moreover, fewer elements (Al, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, V, and Zn) were measured on the stone surfaces, so that the sensitivity was improved by prolonging the dwell times used. The ablation set-up for each stone consisted of 5 separate lines of 3 cm in length, with the starting position 1 cm from each edge (Fig. S3).

### 2.3. Statistical analysis

Apportionment of different carbonaceous aerosol components to their sources relies on a specific information available in the measured dataset. The concentration of OC was derived from a difference between the TC and BC concentrations. Moreover, spectrally resolved optical absorption measurements differentiate between different BC sources (from traffic – $BC_{ff}$ and from biomass burning – $BC_{bb}$), and between BC and BrC absorption. The EC (BC) tracer model was used to split OC into primary (POC) and secondary (SOC). Similarly, the modified BC tracer model was used to further split between primary ($POA_{BrC}$) and secondary BrC ($SOA_{BrC}$), where different values of mass absorption coefficient (MAC) were used to calculate the eqivalent mass of primary and secondary BrC ($MAC_{BrC,prim} = 5.5\ m^2\ g^{-1}$ and $MAC_{BrC,sec} = 2.4\ m^2\ g^{-1}$). A constant, season-independent factors of $POA/POC = 1.2$ and $SOA/SOC = 1.8$ were applied to convert the carbon mass into the aerosol mass. In the last step, aerosol mass concentration of non-light-absorbing aerosols was estimated using a mass closure ($POA = POA_{non\text{-}abs} + POA_{BrC}$ for primary organic aerosols and $SOA = SOA_{non\text{-}abs} + SOA_{BrC}$ for secondary organic aerosols, respectively). Workflow is presented in Scheme 1 and detailed methodology in the work of Ivančič et al. (2022).

Source apportionment of $PM_{2.5}$ was performed using a PMF receptor model applied with the EPA-PMF5 software. The EPA PMF5 software has been widely applied to the characterization of PM sources (Belis et al., 2020; Cesari et al., 2016). It is based on a multi-linear engine (ME) that allows for the application of specific constraints to PMF outputs (Paatero et al., 2014). The dataset used as an input included particulate ions, elements, OC, $BC_{ff}$, and $BC_{bb}$. Considering the Signal-to-Noise (S/N) criteria and the number of data above the detection limit, input variables of fluoride, lactate, and nitrite were classified as "bad" and were not included in the PMF analysis. All the other variables were classified as "strong". This resulted in a dataset of 69 samples with 26 chemical species as input parameters including $PM_{2.5}$ used as the total variable. Different runs were carried out with different number of factors and the best solution was obtained with six factors representing six different sources. PMF5 was applied using specific constraints on factor profiles in order to limit rotational ambiguity and obtain more interpretable source profiles. Specifically, in the road traffic factor/source constraints were applied to $BC_{ff}$ (pull up maximally) and $BC_{bb}$ (pull down maximally). The expectation value (Q) of each constraint was within 1 % and the final Q-value obtained with respect to the base run was 0.5 %. The uncertainties on the profiles and the contributions of the different factors were evaluated using the bootstrap method (Paatero et al., 2014) in terms of one standard deviation.

Images resulting from the 2D elemental analysis of PM filters with LA-ICPMS were processed as described in Ogrizek et al. (2021). For the intercomparison between different campaigns, elemental and ionic composition results were analysed as described for stone samples. For the analysis of stone surface deposits, background signal was first subtracted from gas blank and outlier pixels were removed (the rule of three interquartile ranges was applied, same as for PM samples; see Ogrizek et al. (2021)). An average of every line was considered one unit in this case. Elemental composition results were compared as follows: (i) every exposure stone was compared with a blank stone sample, (ii) for every campaign, sheltered and unsheltered treatments were compared, and (iii) different campaigns were compared with each other. For the basic overview over the working dataset, the Shapiro-Wilk test was performed, as well as the Q-Q plot for assessing the normality and Levene's test for testing the equality of variances. Since the majority of data was not normally distributed and/or did not exhibit equal variances, a non-parametrical statistical test was selected for statistical evaluation. Mann-Whitney test was used to investigate differences between two sample groups (*i.e.* to compare every sample with a blank or compare sheltered to unsheltered samples). The comparison of seasonal campaigns (*i.e.* to obtain differences between multiple groups) was made with use of the Kruskal-Wallis and Dunn's *post hoc* test. Benjamini & Hochberg *p*-value adjustment method was applied in all multiple comparisons. Statistical analysis was performed using program R with raster, data.table, reshape2 (Wickham, 2007), tidyverse (Wickham et al., 2019), rstatix, and ggpubr packages.

## 3. Results and discussion

### 3.1. Characterization and source apportionment of atmospheric aerosols in different seasons

Atmospheric total particle number concentration (TPC) in the size range of 14–750 nm, TC and BC were measured in near-real time. Typical diurnal profiles (Fig. S4) exhibit bimodal shape peaking in the morning and at night, which is associated with the dynamics of the atmospheric mixed layer and diurnal emission patterns (*e.g.*, rush-hour) (Manning et al., 2018). Bimodality is especially pronounced in winter, which can be attributed to morning temperature inversion common for the Ljubljana basin. During temperature inversion, the height of the mixing layer is substantially reduced and concentrations of primary pollutants that are trapped within this relatively narrow layer of air consequently increase. Note that in February 2021 there was a lot of sun, which is needed for this meteorological phenomenon.

Time series of TPC, TC and BC are shown in Fig. S4. Except for some momentary BC spikes, fair agreement is observed between the three parameters in all seasons. This can be attributed to predominant traffic emissions as a constant pollution source in the city. As regards the spikes, careful examination of the corresponding contour plots revealed a sudden income of relatively large carbonaceous aerosols, *i.e.* bigger than the diameter at which total number concentrations peaked (*i.e.* at 60–100 nm). These particles did not contribute much to the total number concentration, while they increased particle mass significantly, which is thus only observed in the TC and BC parts of the time series. In general, much higher TPC, TC and BC concentrations are characteristic of cold seasons compared to the warmer months (by roughly a factor of two).

Airborne concentrations of selected elements in all five seasonal campaigns are presented and compared in Fig. S5. For K, Mg, Na, and Tl quantification was not possible; therefore, their relative contributions as measured by LA-ICPMS are additionally shown in Fig. S6. Based on the obtained seasonal pattern, a quick inspection divides the elements into two groups: i) those enriched in colder months (autumn and winter; *e.g.* As, Cd, Cr, Mn, Mo, Pb, Rb, Zn) are characteristic of fossil-fuel combustion emissions, whereas ii) those with higher concentrations and scattering observed in February and June 2021 (*e.g.* Al, As, Co, Fe, Mn, Rb, V, also K, Mg, Na, Tl) can be attributed to Saharan dust events that were reported in the respective periods of time (23.–26.2.2021 and 21.–24.6.2021).

Characteristic seasonal patterns were also observed for chloride, nitrate, and methanesulfonate (Fig. S7). Nitrate and chloride concentrations peak in autumn and winter, which can be attributed to wood combustion for heating purposes. Methanesulfonic acid, on the other hand, is one of the most important secondary organic aerosol components in marine environments. It is the oxidation product of gaseous dimethylsulfide that is emitted from the ocean due to phytoplankton activity especially in warmer months (Mansour et al., 2020). Methanesulfonate was indeed predominant in PM collected in the spring and summer campaigns.

Carbonaceous aerosol source apportionment plots are shown in Fig. 2. In autumn and winter, biomass-burning emissions contributed substantially ($BC_{bb}$ and absorbing primary organic aerosols – $POA_{BrC}$), while the contribution of SOA was minor in this time of the year. In summer, SOA represents more than half of the total carbonaceous aerosol mass, which is due to pronounced photochemistry, while BrC aerosols only contribute a small portion of it, during daytime. Non-absorbing aerosols ($POA_{non\text{-}abs}$ + $SOA_{non\text{-}abs}$) represent roughly 60–80 % of the carbonaceous aerosol mass in summer. Although we conducted a campaign already in very late spring, there is still some evidence of biomass-burning emissions, probably due to agricultural waste burning. The contribution of non-absorbing aerosols in spring was similar to the summer periods. Traffic emissions tend to be relatively constant throughout the year and stabilized somewhere below 20 % of the carbonaceous aerosol mass. It should be noted at this point that especially autumn and winter campaigns were affected by restrictions due to the coronavirus pandemic, which could result in lower-than-usual traffic emissions in these seasons (only slightly higher absolute $BC_{ff}$ concentrations were determined in the cold seasons compared to the warmer months).

Combining elemental and ionic composition (airborne concentrations are reported in Table S2 and Table S4), OC and BC content, PMF analysis was further performed and confirmed traffic as the main PM pollution source in Ljubljana, Slovenia, contributing with 30 % to the investigated $PM_{2.5}$ mass. Similar has been observed by Saraga et al. (2021). The other factors, which together with traffic accounted for roughly 96 % of the analysed PM, are: secondary inorganic aerosols (nitrate (15 %) and sulphate (18 %)), biomass burning (14 %), mineral dust (12 %), and marine-rich biogenic SOA (7 %). Relative source contributions are given in Fig. 3, while the profiles of the different factors are reported in Fig. S8.

Nitrate (factor 1) and sulphate (factor 4), as indicators of inorganic secondary atmospheric aerosols that may have travelled long distances, are characteristic of different seasons, *i.e.* winter and summer, respectively. While sulphate is typically linked with photochemistry and thus accompanied with SOA (*e.g.* oxalate), winter nitrate can be attributed to combustion emissions due to heating purposes (including biomass burning). Correspondingly, biomass burning factor 2 ($BC_{bb}$, phosphate, chloride, Cd, Pb, OC *etc.*) predominates in colder months (domestic heating), whereas isolated events can also be identified in other periods of time (agricultural activities, eventually natural fires). Factor 6 represents a contribution related to biogenic SOA, strongly enriched with methanesulfonate and accompanied with sulphate and oxalate. Therefore, this factor is indicated as biogenic SOA likely of marine origin as also found in other areas (Srivastava et al., 2019). Three special events characterized by huge amounts of crustal elements (Al, As, Ba, Co, Cr, Fe, Mn, Rb, V) are described with factor 3, which were confirmed with the advection of Saharan dust in the region. The most constant PM emission source throughout the year is traffic (factor 5), which is especially enriched with metals, such as Ba, Co, Cu, Fe, Mo, Ni, Sb, V, Zn, and $BC_{ff}$.

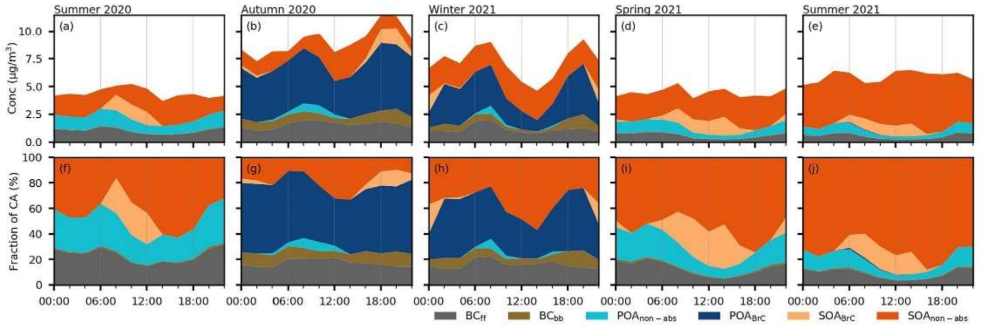


**Fig. 2.** Apportionment of carbonaceous aerosols to different sources in five seasonal campaigns conducted in Ljubljana, Slovenia (summer – August 2020; autumn – November 2020; winter – February 2021; spring – May-June 2021; summer – June-July 2021); black carbon from traffic ($BC_{ff}$) and biomass burning ($BC_{bb}$), non-absorbing and absorbing primary organic aerosols ($POA_{non\text{-}abs}$ and $POA_{BrC}$), and non-absorbing and absorbing secondary organic aerosols ($SOA_{non\text{-}abs}$ and $SOA_{BrC}$).

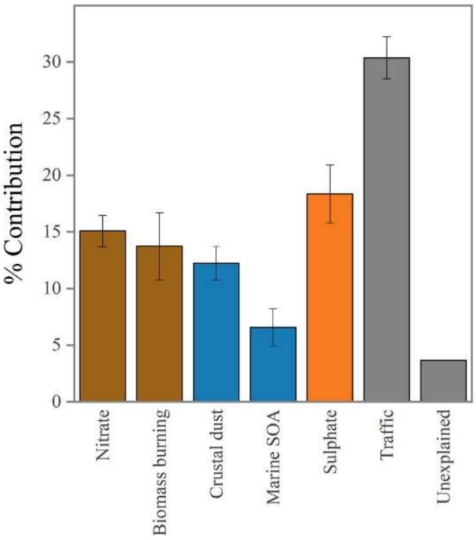


**Fig. 3.** Relative contribution of sources to the investigated $PM_{2.5}$ samples; six PMF factors were identified, unexplained refers to the fraction of $PM_{2.5}$ which could not be reconstructed by the PMF model (~4 %). Typical winter sources are coloured brown, summer orange, in blue are special events that can potentially occur at any time of the year and in grey we represent sources that were rather constant throughout the year.

### 3.2. Correlation between air pollution and stone surface deposits

Stone surfaces were analysed for their elemental composition in a similar way as $PM_{2.5}$ on the filters. Although we optimized LA-ICPMS measurement conditions for the sole ablation of PM deposits, ablation of the underlying stone could not be completely avoided. Therefore, we first compare the exposed samples with their (clean) blanks. In Fig. S9 we can see that the amount of Cd on the exposed stones is not statistically different from the blanks. Moreover, crustal elements in the stone matrix (such as Mg, Mn and Na) hindered their accurate quantification in PM deposits. Lower amounts of these elements were sometimes measured in the exposed samples compared to blanks, which could result from the surface erosion due to weathering and soluble minerals dissolution, but also from the measurement error because of high blank signals.

Although surface analysis was difficult due to trace concentrations and besides, removal processes also influence deposits, a general agreement was found between airborne $PM_{2.5}$ concentrations and PM deposits on the stones. One such example is shown in Fig. 4 for Zn and Al on the sheltered marble samples. Zinc is connected with fossil-fuel combustion, and is thus a typical winter pollutant, which is evident from both, $PM_{2.5}$ and deposit measurements. On the other hand, Al is one of the crustal elements and was thus especially enriched during the Saharan dust events. It should be noted, however, that coarse particles (*i.e.* those bigger than 2.5 μm) also influenced surface deposits compared to the filter results, which is discussed below. Moreover, the winter measurement campaign was a bit delayed with respect to the stone exposure, for which reason the mineral dust storm only affected PM filter results and not stone surface deposits. This is nicely seen in the dataset.

Although seasonality of the deposits was poorly pronounced and depended on the element, we were able to statistically confirm some differences between the exposed stones (Fig. S10). Two characteristic features could be identified in the elemental fingerprint of stone surfaces that deserve special attention. Autumn enrichment in Mg, Mn, Na and Pb does not correlate with airborne measurements (except for Pb) and points to the contamination with soil, which indeed usually contributes to the coarse PM fraction and not $PM_{2.5}$. We attribute these observations to gardening on the terrace where passive collectors were installed. The exception is Pb, which can be linked with another PM source, that is road dust resuspension. On the other hand, huge amounts of Al, Fe, K, Mg, Mn, Na and V in summer samples can be linked with the Saharan dust advection, which correlates well also with the measured airborne $PM_{2.5}$ compositions.

These elemental analysis results are further supported by microscopy. Especially the sheltered marble stone from the autumn campaign was full of halite crystals (Na, Cl), many of which must have crystalized after PM deposition with the interference of some other (carbonaceous) material that made crystals grow into irregular shapes (Fig. 5a). On the other hand, on the surface of the sheltered limestone from the summer campaign, a plethora of coarse spherical particles that resembled biological pollen were found (Fig. 5b). However, their composition (Si, Al, Fe) pointed to the fossilized diatoms or their auxospores, which are typical of desert depressions such as Bodélé Depression of the Sahara Desert (Assmy et al., 2008; Todd et al., 2007). All of these particles are coarse mode and did not contribute to our airborne $PM_{2.5}$ concentrations, which explains the lack of agreement

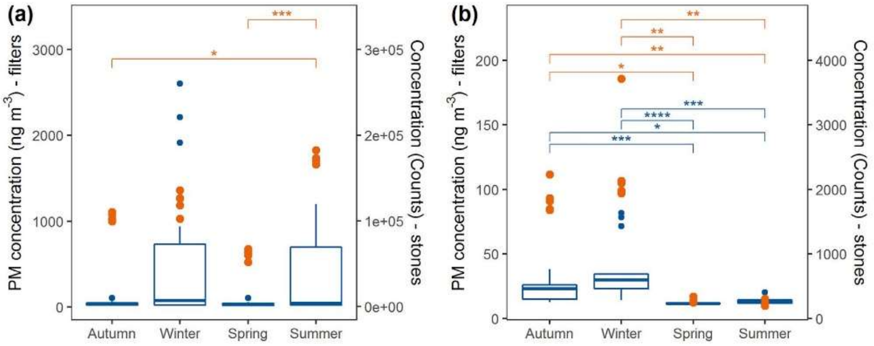


**Fig. 4.** Airborne (blue) *vs.* surface deposit (orange) concentrations of a) Al and b) Zn in four different seasons (November 2020–July 2021). Winter stones were not subjected to the air masses from Sahara, which substantially influenced concentrations of crustal elements on the filters. Statistically significant differences ($p < 0.05$) are marked with asterisk (the more asterisks the more significant the difference).

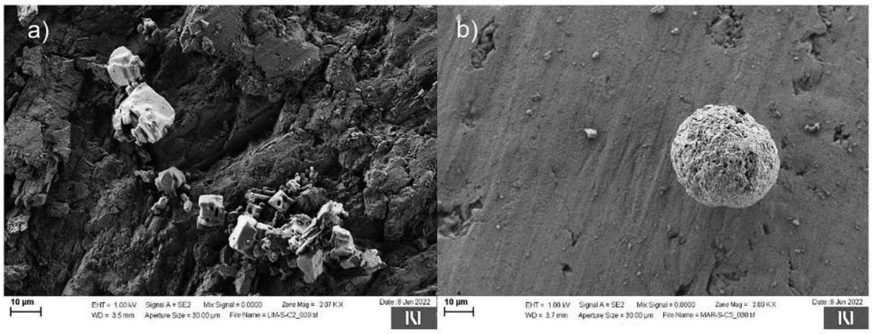


**Fig. 5.** SEM image of a) irregular halite crystals on a sheltered marble (Na, Cl, C) and b) diatomaceous earth/auxospore on a sheltered limestone (Si, Al, Fe, Mg, K).

between PM and surface concentrations for these particular elements. Moreover, large particles are very easily removed and are not expected to contribute to surface deposits in the long run.

When sheltered and unsheltered exposure positions are compared (Table S5), less significant differences are found in the case of more heterogeneous limestone samples with more impurities in their original matrix. In general, however, sheltered stones exhibited higher surface concentrations of the measured elements than unsheltered stones exposed concomitantly. This stems from the comparable PM deposition and limited removal processes in the case of sheltered positions, while unsheltered stones were rain-washed at least once during every campaign. Although one sample set was exposed four-times, in all four consecutive campaigns, their elemental content rarely exceeded all the other four seasonal exposures (see Fig. S10), even in the sheltered position. This points to the importance of diverse removal processes, besides rainfall.

### 3.3. Surface reflectance measurements

Reflectance measurements were evaluated in the CIELAB colour space in order to distinguish between BC, a typical traffic-related pollutant emitted in the atmosphere throughout the year, and biomass-burning related BrC aerosol impacts peaking in cold seasons. The colour space uses L* for lightness, and a* and b* indicate the four complementary colours of the human vision (red–green and yellow–blue axes, respectively). While BC is known to absorb light in the whole visible range, wavelength-dependent light absorption is characteristic of BrC and increases towards the UV range. Therefore, BrC compounds (as well as BrC particles) are typically yellow-to-brown, which could reflect on a surface they deposit on, if only the surface coverage is sufficient. This may cause changes of a* and b*.

Reflectance data for marble and limestone samples before and after the exposure in four seasonal campaigns in sheltered and unsheltered positions are shown in Table S6. First, *L** is considered as a measure of soiling. In the case of unsheltered white marble stones, significant difference was mostly detected between blank and exposed stones (except in winter). However, surface lightness is increased and not decreased, which cannot be attributed to the deposition of absorbing (BC) particles. Stone whitening was also observed on almost all limestone samples that are originally greyish in colour. As bleaching does not seem to correlate with ambient particle concentrations in different seasons, non-absorbing aerosol deposition is not expected to contribute in these short-term exposures. In fact, stone bleaching is usually attributed to optical effects due to weathering effects, as a consequence of changes in the surface roughness (Marszałek and Skowroński, 2010).

Although BrC concentrations varied much more through the year than the level of BC pollution, no significant colour changes were measured for any of the samples exposed in one-month campaigns that could be correlated with seasonal PM composition.

Besides one-month exposures, one set of stones was also exposed in all four seasonal campaigns (Table S7). In this case, initial bleaching followed by a gradual darkening of the surface was observed (except for the sheltered limestone), which could be related to PM deposition (soiling). Again, the colour of marble did not change significantly during the exposure, whereas limestone exhibited more blue tones after all four campaigns (for both, sheltered and unsheltered positions). None of the analysed stones, however, reflected in the yellow-red regions, which are typical of BrC components.

Although we cannot draw conclusions about BrC soiling based on the monthly exposure data, the methodology seems appropriate for long-term exposure studies which are ongoing in the laboratory, as air quality data confirmed predomination of BrC particles over BC in the atmosphere. BrC aerosols accounted for up to 60 % carbonaceous aerosol mass in the colder part of the year (with minor contribution in summer), while BC remained below 20 % in all seasons. However, the bigger PM amount does not necessarily reflect in increased soiling, since optical characteristics play an equally important role in the cumulative effect as the concentration.

Therefore, in Fig. 6 we further compare optical absorption of measured carbonaceous aerosols by BC and BrC at 370 nm. The data show that BC absorption still exceeds BrC absorption in all seasons and the difference in

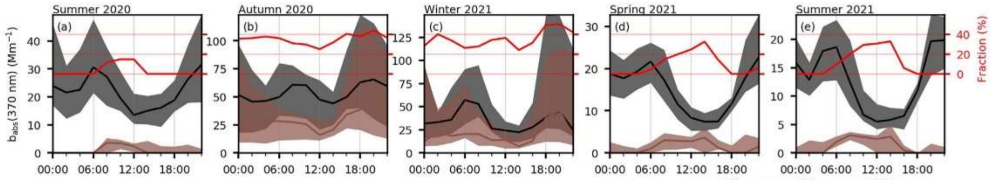


**Fig. 6.** Seasonal diurnal profiles of optical absorption by the measured black carbon ($b_{\mathrm{abs}}^{\mathrm{BC}}$) and brown carbon ($b_{\mathrm{abs}}^{\mathrm{BrC}}$) at 370 nm: median, Q1 and Q3.

absorption is expected to be even bigger in the visible range of the spectrum. Nevertheless, with applying BC limits at the national level and more rigorous preventive measures for BC abatement, the situation may change already in the near future.

## 4. Conclusions

We can conclude that fresh PM deposits on calcareous stone surfaces roughly resemble the composition of airborne PM; the higher the exposure to a particular pollutant, the bigger its amount on the stone surface in the short run. In this sense, more polluted seasons and areas pose a bigger treat to stone heritage objects, especially when it comes to fast corrosion processes. On the other hand, we also show that particulate accumulates do not simply sum up in the long run. Therefore, linear extrapolation from short-term exposures could lead to erroneous prediction results. Although sheltering protects stone surfaces from wet removal processes (*e.g.* rain wash, dew), other removal processes such as surface-wind interaction seem comparably important when considering PM accumulation on a surface.

Due to opposing effects of stone weathering causing optical whitening of the surface and soiling, absorbing aerosol deposition could not be evaluated in the performed 1-month campaigns. Nevertheless, we show that BC absorption exceeded BrC absorption at 370 nm in all seasons, which confirms BC is still a predominant soiling factor in urban sites like Ljubljana, Slovenia. This, however, can change in less polluted environments and in the future, once BC emissions will be successfully mitigated.

In this study we advance a holistic methodological approach of other groups (*e.g.* Fermo et al. (2015); Winkler et al. (2022)) to studying PM deposition, aging and removal processes on calcareous stone surfaces as well as stone surface degradation with non- and micro-destructive techniques, which can help predict the fate of cultural heritage objects in polluted environments and adopt most suitable mitigation measures.

## CRediT authorship contribution statement

**Monika Ogrizek:** Investigation, Formal analysis, Writing – review & editing, Visualization. **Asta Gregorič:** Data curation, Formal analysis, Writing – review & editing. **Matic Ivančič:** Formal analysis, Visualization. **Daniele Contini:** Resources, Formal analysis, Writing – review & editing. **Urša Skube:** Investigation, Formal analysis. **Kristijan Vidović:** Methodology, Investigation. **Marjan Bele:** Investigation. **Martin Šala:** Investigation. **Marta Klanjšek Gunde:** Resources. **Martin Rigler:** Resources. **Eva Menart:** Conceptualization. **Ana Kroflič:** Conceptualization, Writing – original draft, Visualization, Project administration, Funding acquisition.

## Data availability

Data will be made available on request.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Asta Gregorič, Matic Ivančič and Martin Rigler are employed by the company Aerosol d.o.o., which develops and manufactures aerosol instrumentation, including the CASS instrument used in the campaigns.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.159012.

## References

Akos, T., Licha, T., Simon, K., Siegesmund, S., 2011. Urban and rural limestone weathering; the contribution of dust to black crust formation. Environ. Earth Sci. 63, 675–693.

Assmy, P., Hernandez-Becerril, D.U., Montresor, M., 2008. Morphological variability and life cycle traits of the type species of the diatom genus Chaetoceros, C-dichaeta. Journal of Phycology 44, 152–163.

Belis, C.A., Pernigotti, D., Pirovano, G., Favez, O., Jaffrezo, J.L., Kuenen, J., et al., 2020. Evaluation of receptor and chemical transport models for PM10 source apportionment. Atmos. Environ. X 5, 100053.

Bonazza, A., Sabbioni, C., Ghedini, N., 2005. Quantitative data on carbon fractions in interpretation of black crusts and soiling on european built heritage. Atmos. Environ. 39, 2607–2618.

Bonazza, A., Messina, P., Sabbioni, C., Grossi, C.M., Brimblecombe, P., 2009. Mapping the impact of climate change on surface recession of carbonate buildings in Europe. Sci. Total Environ. 407, 2039–2050.

Brimblecombe, P., Grossi, C.M., 2005. Aesthetic thresholds and blackening of stone buildings. Sci. Total Environ. 349, 175–189.

Calparsoro, E., Maguregui, M., Giakoumaki, A., Morillas, H., Madariaga, J.M., 2017. Evaluation of black crust formation and soiling process on historical buildings from the Bilbao metropolitan area (north of Spain) using SEM-EDS and raman microscopy. Environ. Sci. Pollut. Res. 24, 9468–9480.

Cesari, D., Donateo, A., Conte, M., Contini, D., 2016. Inter-comparison of source apportionment of PM10 using PMF and CMB in three sites nearby an industrial area in Central Italy. Atmos. Res. 182, 282–293.

De Marco, A., Screpanti, A., Mircea, M., Piersanti, A., Proietti, C., Fornasier, M.F., 2017. High resolution estimates of the corrosion risk for cultural heritage in Italy. Environ. Pollut. 226, 260–267.

Di Turo, F., Proietti, C., Screpanti, A., Fornasier, M.F., Cionni, I., Favero, G., et al., 2016. Impacts of air pollution on cultural heritage corrosion at European level: what has been achieved and what are the future scenarios. Environ. Pollut. 218, 586–594.

Drinovec, L., Mocnik, G., Zotter, P., Prevot, A.S.H., Ruckstuhl, C., Coz, E., et al., 2015. The "dual-spot" aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation. Atmos. Meas. Techn. 8, 1965–1979.

Fermo, P., Turrion, R.G., Rosa, M., Omegna, A., 2015. A new approach to assess the chemical composition of powder deposits damaging the stone surfaces of historical monuments. Environ. Sci. Pollut. Res. 22, 6262–6270.

Fermo, P., Goidanich, S., Comite, V., Toniolo, L., Gulotta, D., 2018. Study and characterization of environmental deposition on marble and surrogate substrates at a monumental heritage site. Geosciences 8.

Giavarini, C., Santarelli, M.L., Natalini, R., Freddi, F., 2008. A non-linear model of sulphation of porous stones: numerical simulations and preliminary laboratory assessments. J. Cult. Herit. 9, 14–22.

Giussani, B., Monticelli, D., Rampazzi, L., 2009. Role of laser ablation-inductively coupled plasma-mass spectrometry in cultural heritage research: a review. Anal. Chim. Acta 635, 6–21.

Ivančič, M., Geregorič, A., Lavrič, G., Alföldy, B., Ježek, I., Hasheminassab, S., et al., 2022. Two-year-long high-time-resolution apportionment of primary and secondary carbonaceous aerosols in the Los Angeles Basin using an advanced total carbon–black carbon (TC-BC(λ)) method. Sci. Total Environ. 848, 157606.

Kušan, A.C., Kroflič, A., Grgić, I., Ciglenečki, I., Frka, S., 2020. Chemical characterization of fine aerosols in respect to water-soluble ions at the eastern middle adriatic coast. Environ. Sci. Pollut. Res. 27, 10249–10264.

Laskin, A., Laskin, J., Nizkorodov, S.A., 2015. Chemistry of atmospheric brown carbon. Chem. Rev. 115, 4335–4382.

Lombardo, T., Ionescu, A., Chabas, A., Lefevre, R.A., Ausset, P., Candau, Y., 2010. Dose-response function for the soiling of silica-soda-lime glass due to dry deposition. Sci. Total Environ. 408, 976–984.

Manning, M.I., Martin, R.V., Hasenkopf, C., Flasher, J., Li, C., 2018. Diurnal patterns in global fine particulate matter concentration. Environ. Sci. Technol. Lett. 5, 687–691.

Mansour, K., Decesari, S., Bellacicco, M., Marullo, S., Santoleri, R., Bonasoni, P., et al., 2020. Particulate methanesulfonic acid over the Central Mediterranean Sea: source region identification and relationship with phytoplankton activity. Atmos. Res. 237, 104837.

Marszałek, M., Skowroński, A., 2010. Black "marble": The characteristic material in the baroque architecture of Cracow (Poland). In: Dan, M.B., Přikryl, R., Török, Á. (Eds.), Materials, Technologies and Practice in Historic Heritage Structures. Springer Netherlands, Dordrecht, pp. 93–106.

Martinsson, J., Sporre, M.K., Pedehontaa-Hiaa, G., Azeem, H.A., 2020. On the relationship of biogenic primary and secondary organic aerosol tracer compounds on the aethalometer model parameters. Aerosol Air Qual. Res. 20, 2654–2668.

Ogrizek, M., Jaćimović, R., Šala, M., Kroflič, A., 2021. No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters. Talanta 226, 122110.

Ogrizek, M., Kroflic, A., Sala, M., 2022. Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter. Trends in environmentalAnal. Chem. 33.

Ozga, I., Ghedini, N., Giosue, C., Sabbioni, C., Tittarelli, F., Bonazza, A., 2014. Assessment of air pollutant sources in the deposit on monuments by multivariate analysis. Sci. Total Environ. 490, 776–784.

Paatero, P., Eberly, S., Brown, S.G., Norris, G.A., 2014. Methods for estimating uncertainty in factor analytic solutions. Atmos. Meas. Techn. 7, 781–797.

Rigler, M., Drinovec, L., Lavric, G., Vlachou, A., Prevot, A.S.H., Jaffrezo, J.L., et al., 2020. The new instrument using a TC-BC (total carbon-black carbon) method for the online measurement of carbonaceous aerosols. Atmos. Meas. Techn. 13, 4333–4351.

Saiz-Jimenez, C., 1993. Deposition of airborne organic pollutants on historic buildings. Atmos. Environ. BUrban Atmos. 27, 77–85.

Saraga, D., Maggos, T., Degrendele, C., Klanova, J., Horvat, M., Kocman, D., et al., 2021. Multi-city comparative PM2.5 source apportionment for fifteen sites in Europe: the ICARUS project. Sci. Total Environ. 751.

Srivastava, D., Favez, O., Petit, J.E., Zhang, Y., Sofowote, U.M., Hopke, P.K., et al., 2019. Speciation of organic fractions does matter for aerosol source apportionment. Part 3: combining off-line and on-line measurements. Sci. Total Environ. 690, 944–955.

Tidblad, J., Kucera, V., Ferm, M., Kreislova, K., Brüggerhoff, S., Doytchinov, S., et al., 2012. Effects of air pollution on materials and cultural heritage: ICP materials celebrates 25 years of research. Int. J. Corros. 2012, 496321.

Todd, M.C., Washington, R., Martins, J.V., Dubovik, O., Lizcano, G., et al., M'Bainayel, S., 2007. Mineral dust emission from the Bodele Depression, northern Chad, during BoDEx 2005. Journal of Geophysical Research-Atmospheres 112.

Vidović, K., Hočevar, S., Menart, E., Drventić, I., Grgić, I., Kroflič, A., 2022. Impact of air pollution on outdoor cultural heritage objects and decoding the role of particulate matter: a critical review. Environ. Sci. Pollut. Res. 29, 46405–46437.

Wickham, H., 2007. Reshaping data with the reshape package. J. Stat. Softw. 21, 1–20.

Wickham, H., Averick, M., Bryan, J., Chang, W., McGowan, L.D.A., François, R., et al., 2019. Welcome to the tidyverse. J. Open Source Softw. 4, 1686.

Winkler, A., Contardo, T., Lapenta, V., Sgamellotti, A., Loppi, S., 2022. Assessing the impact of vehicular particulate matter on cultural heritage by magnetic biomonitoring at Villa Farnesina in Rome, Italy. Sci. Total Environ. 823.

## 3.5 Article 5: Determination of Trace Concentration of Simple Phenols in Ambient PM Samples

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Simple phenols (*e.g.* phenol, catechol, guaiacol, cresol) are emitted in the air mostly during biomass burning and by traffic. They are toxic by themselves, however in the atmosphere, they can act as precursors and be transformed to secondary phenols (*e.g.* by nitration, oxidation), which are often more stable and more harmful for the environment (*e.g.* forming BrC) and health (*e.g.* nitrophenols). Even though they are produced from the most widespread anthropogenic sources, they are usually not measured in PM, since their determination with GC/LC-MS is hindered by the semi-volatile character, limited water solubility, poorly ionizable functional groups, and trace concentrations.

The article presents an LC-MS/MS method developed for the determination of simple phenols in PM samples, by previous sample extraction and derivatization reaction using DnsCl. The method does not include any pre-concentration step, which could result in a loss of semi-volatile analytes.

During the method development, every step was carefully assessed to provide the highest responses possible. Reaction conditions were optimized for the highest derivatization efficiency specifically for the targeted analytes (*e.g.* solvent, buffer pH and strength, reaction time and temperature, mixing conditions, and DnsCl concentration), whereas HPLC mobile phases, columns and elution gradient were optimized for the best analyte separation, and electrospray ionization (ESI)-MS/MS parameters for the highest possible peak intensity, together with selective identification of analytes by specific identification ions. The method was carefully validated in terms of extraction efficiency, derivatization repeatability and product stability, blanks and robustness, precision, LOD, linearity, measuring range, selectivity, and specificity of the measurement method. At the end, seven winter and five spring ambient $PM_{2.5}$ samples were measured, which were collected on a terrace of the National Institute of Chemistry and carefully handled before the analysis (stored in a freezer) to minimize the loss of semi-volatile components.

The developed method showed very good performance characteristics, such as very low LOD below 0.2 ng $mL^{-1}$, precision within 10 % (except for catechol it was 18 %), sufficient linearity range, a limited number of interferences (only *p*- and *m*-cresol interference were identified), and robustness with long-term stability of derivatized analytes.

The analyzed PM samples exhibited the expected seasonal trend, with higher concentrations in winter due to biomass burning for heating purposes, whereas we measured the highest phenolic concentrations in the sample with the lowest average daily temperature, which can be explained with a larger amount of biomass burned for maintaining the indoor temperature. The highest concentrations were measured for catechol, determination of which was found sensitive to the presence of metals in the sample. Due to the formation of catechol-metal complexes, therefore, the addition of ethylenediaminetetraacetic acid (EDTA) is recommended, which binds divalent metals and restores catechol in its native form. On the other hand, phenolic concentration in the summer samples was mostly below LOD, which could be both due to the absence of biomass burning in that period and/or due to climatic conditions as is higher temperature causing the distribution of semi-volatiles into the gas phase.

We compared our results with previously published data on nitrophenols in the same city [83, 125], which also exhibit the seasonal winter-summer trend and are connected with biomass burning emissions. Correlation was observed in the trends of nitrocatechol-catechol, exhibiting the highest concentrations in both cases, nitrophenol-phenol and nitroguaiacol-guaiacol. Some relations between precursor-secondary compounds were further suggested and with the developed method, more studies can focus on the levels of simple phenols in ambient air, and phenolic precursors can be followed in fundamental kinetic studies helping to understand reaction mechanisms in the atmosphere and formation of secondary compounds.

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# Determination of trace concentrations of simple phenols in ambient PM samples

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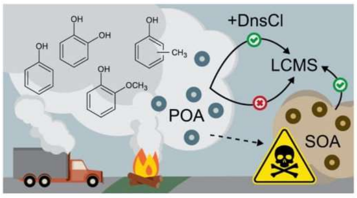
## HIGHLIGHTS

- Phenol dansylation improves ionization and enables LC-MS analysis.
- Optimal reaction and measuring parameters provide very low limits of detection.
- Phenol, catechol, guaiacol and cresol are determined in ambient particulate matter.
- Concentrations of simple phenols in particulate matter are low, peaking in winter.
- Simple phenols can be precursors to toxic secondary aerosols (*e.g.* nitrophenols).

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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*Keywords:*
Particulate matter
Simple phenols
LC-MS
Dansyl chloride
Guaiacol
Catechol

## ABSTRACT

Phenols are hazardous, but yet ubiquitous in the environment, including in atmospheric aerosols due to combustion emissions. There, phenols are subjected to secondary transformations, producing even more toxic nitrophenolic air pollutants. However, primary simple phenols, i.e. those containing only hydroxyl, methyl and methoxy substituents are not easy to detect. Trace concentrations, semi-volatile character and poorly ionizable functional groups prevent us from their determination by the most common analytical techniques, such as gas and liquid chromatography with mass spectrometric detection (GC/LC-MS). Here, we present a new derivatization method for MS/MS detection with positive ion electrospray ionization (+ESI-MS/MS) of simple phenols in atmospheric particulate matter (PM) extracts. The method is sensitive, selective, and robust, and requires no sample concentration step, which is critical due to the volatile character of the target analytes. After derivatization with dansyl chloride, phenol, catechol, cresols and guaiacol were detected in urban PM samples from Ljubljana, Slovenia. This method finally enables to study the abundance of primary phenols in atmospheric PM from different sources, which will improve understanding of secondary aerosol (trans)formation pathways and allow for more targeted mitigation strategies in respect to airborne phenolic pollutants.

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## Authors contributions

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## 1. Introduction

Phenols are known toxic compounds causing respiratory tract irritation (United States Environmental Protection Agency, EPA). For phenol, PHE, and different isomeric cresols (methylphenols), CRE, effects on the blood, liver, kidney, central nervous system, and reduced body weight have been reported in animal studies (EPA). Furthermore, CRE and catechol (1,2-dihydroxybenzene), CAT, are even classified as possible human carcinogens (EPA; International Agency for Research on Cancer, IARC) and PHE, CAT, and CRE are listed on the Hazardous Air Pollutants list (EPA, 2005).

Phenols (*i.e.* compounds possessing a hydroxybenzene moiety) are abundant in the air mostly due to anthropogenic activities, as are traffic and biomass burning. In the atmosphere, semi-volatile phenols are found in the gaseous phase or bound to particulate matter (PM). They can be emitted as primary aerosols (mostly phenols originating from wood lignin) or secondary aerosols formed from *e.g.* benzene, toluene, and anisole in reactions with the atmospheric $OH^{\bullet}$ produced from the same sources (Pillar and Guzman, 2017). Although simple phenols are considered predominantly gaseous pollutants, Campen et al. (2014) showed that total engine emissions (including PM and volatile pollutants) are more toxic than the PM or the gaseous phase alone. Moreover, simple phenols can be precursors to even more toxic nitrated mono-aromatic compounds (Pillar and Guzman, 2017; Finewax et al., 2018; Kroflič et al., 2021; Feng-Yang et al., 2022) or secondary organic aerosol (SOA)-forming hydroxylated phenols (He et al., 2019), which are among others typical constituents of atmospheric brown carbon and consequently influence Earth's radiative forcing and induce global warming.

Characterization and monitoring of atmospheric phenols, in the gaseous phase and PM, are among the first steps to mitigating the concentrations of these toxic compounds in the air. Their determination in both atmospheric phases would further contribute to more accurate source identification and improve understanding of secondary aerosol formation in the atmosphere, which is the major uncertainty in atmospheric models (Intergovernmental Panel on Climate Change, IPCC, 2013). Although many researches include gas-phase phenol monitoring (Pistonesi et al., 2010; Sturaro et al., 2010; Borhan et al., 2012), a sensitive analytical technique for accurate determination of PM-bound phenols in ambient samples is still lacking.

Determination methods for secondary phenols (*e.g.* nitrophenols, carbonyl benzenes) in atmospheric PM are well established; usually, a simple extraction in an organic or aqueous solvent is followed by liquid chromatography-mass spectrometry (LC-MS) analysis (Hoffmann et al., 2007; Kitanovski et al., 2012; Forbes, 2020; Liang et al., 2020; Jakovljević et al., 2021). On the other hand, determination of simple phenols as precursors to nitrophenols and aromatic acids is more complicated and only a few studies have been conducted in this respect. Due to their bipolar character – note relatively high volatility and high water solubility are combined in a single molecule, their determination by standard analytical techniques becomes challenging. The majority of the works have used gas chromatography (GC)-MS for the determination of phenols in ambient PM, however, they either involved samples of very high concentrations (*e.g.* wood stove smoke) (Hawthorne et al., 1989) or included derivatization reactions. In the latter cases, analytical methods have only been applied to blank filters spiked with respective standards (Jaoui et al., 2018), or real samples have been pre-concentrated with evaporation to dryness (Morville et al., 2004) or solid-phase extraction (Moldoveanu and Kiser, 2007). Only two papers report on the usage of high performance LC (HPLC) with UV detection, where no other pre-treatment except extraction was needed; nevertheless, both focused on concentrated samples, either tobacco (Risner and Cash, 1990) or cigarette smoke (Moldoveanu and Kiser, 2007). Typical urban PM samples, however, cannot be analyzed with HPLC-UV/VIS since the sensitivity is likely not adequate and the selectivity is strongly compromised by the sample matrix. These problems are usually overcome by using mass spectrometry as a detection technique (*i.e.* HPLC-MS/MS). Although secondary phenols can be most easily detected by LC-MS with an electrospray ionization (ESI) source, it is not the case with their precursor phenols, at least not at concentration levels expected in ambient PM.

Simple phenols very poorly ionize in typical MS sources, such as ESI or atmospheric pressure chemical ionization (APCI). Enhancement of ionization efficiency can be achieved by tagging analytes with a derivatization agent. Dansyl chloride (DnsCl) is a known derivatization reagent for the phenolic hydroxyl group and it has already been used for the determination of phenols as biomarkers in urine (PHE) (Guo and Li, 2009), river, and sediment samples (PHE, *p*-CRE) (Xu et al., 2021). However, none has provided optimal reaction conditions for PM-relevant phenols, which is necessary for the detection at trace levels. Nevertheless, the use of DnsCl is well established for some other phenolic compounds, such as bisphenol A (Chang et al., 2010; Yang et al., 2011; Wang et al., 2018; Yao et al., 2020), estrogens (Fan et al., 2014; Ferreira et al., 2017), uridine (Chen et al., 2019), and alkylphenols (Pernica et al., 2015) in different environmental and biological samples and for the purpose of phenol submetabolome studies (Zhao et al., 2016; Luo and Li, 2017; Mung and Li, 2017). The dansylation reaction provides repeatable results and can enhance sensitivity by 100-fold (Guo and Li, 2009; Xu et al., 2021), which proves promising also for the determination of phenolic traces in ambient PM samples.

Even though the derivatization reaction has already been established for other analytes and samples, those parameters may not be optimal for ambient PM. DnsCl is reactive toward bases (Gray, 1972), which means that phenol has to be in a deprotonated form in order to react with it. Moreover, labelling of target analytes with DnsCl is always in competition with DnsCl hydrolysis forming Dns-OH (*m/z* 251, data not shown), which accelerates at pH $> 9.5$ and may lead to unsuccessful derivatization due to reagent deactivation (Gray, 1972). Values of pKa for the investigated phenols are in the range of 9.5–10.3 (Table S1) requiring pH around 10 to ensure enough phenolate ions in the reaction mixture for successful derivatization, which is in conflict with Dns deactivation at these conditions. In the case of trace concentrations in PM, however, the highest possible sensitivity is required, which can only be maximized with precise optimization of reaction pH and other relevant parameters.

In this work, we present a method for the determination of target phenols (PHE, CAT, CRE, guaiacol (2-methoxyphenol, GUA)) in atmospheric PM by LC-(ESI)-MS with prior derivatization with DnsCl. Derivatization conditions were optimized and the proposed protocol is validated against the measuring range, linearity, precision, robustness, interferences, and extraction efficiency. In the end, seasonal PM samples from Ljubljana, Slovenia are successfully analyzed.

## 2. Material and methods

### 2.1. Reagents and chemicals

Phenolic standards (PHE, CAT, GUA, *m*-CRE, *p*-CRE, *o*-CRE; purity ≥98%), DnsCl, sodium bicarbonate ($NaHCO_3$), and sodium carbonate ($Na_2CO_3$; suprapur) were purchased from Sigma-Aldrich/Merck (Darmstadt, Germany). Solvents (methanol, MeOH, acetonitrile, ACN) and formic acid, FA, for extraction and mobile phase preparation were used at the required purity for the respective technique. Acetone used for DnsCl dissolution was purchased from Honeywell, Chromasolv™ for pesticide residue analysis. Milli-Q (MQ) water was daily collected fresh from the Millipore purification system (Bedford, MA, USA).

### 2.2. *Sample collection*

Ambient PM samples were collected on the roof of the National Institute of Chemistry (Ljubljana, Slovenia) by a low-volume PM sampler (Giano, Dado Lab) on 47 mm diameter quartz fiber filters (PALL), sampled for 24 h each. Ljubljana is the capital of Slovenia with 287,000 inhabitants. It is representative of an urban environment with predominant traffic emissions, some smaller industrial plants, and domestic combustion emissions as major air pollution sources. The samples were collected in January–February and May–June 2021. Details on the collected samples are summarized in Table S2.

PM mass was determined gravimetrically (Sartorius micro; 1 μg sensitivity), with prior conditioning of the filters for at least 1 day at 20 ± 1 °C and 48 ± 5% relative humidity (according to EN12341:2014). To prevent evaporation of volatile components from the filters, the samples were stored air-tight in a freezer at −20 °C and defrosted before extraction and analysis.

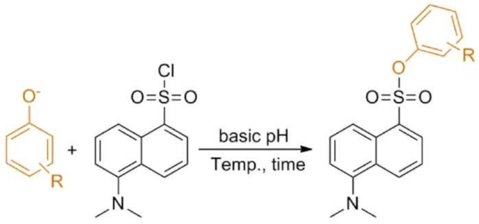
### 2.3. *Stock solutions and PM extracts*

Stock solutions of phenolic standards used for the optimization of derivatization reaction and analysis conditions were prepared by dissolution and/or dilution of solid/liquid standards in different solvents. For details see section 2.4 and Supplementary information, SI, section 2.2.

Ambient PM samples were extracted as described before (Kitanovski et al., 2012; Frka et al., 2016), with minor alterations. After defrosting in a desiccator, a filter subsample (two square punches of 1 cm$^2$, corresponding to 19% of the total sampled area) was taken and cut into small pieces with ceramic scissors. The subsample was extracted with addition of 1 mL 80% ACN in MQ water on an orbital shaker (1 h, 400 rpm, 23 °C). At the end of extraction, broken filter fibers and undissolved particles were removed by filtration through a syringe filter (polytetrafluoroethane (PTFE), 0.45 μm pore size).

### 2.4. *Derivatization reaction*

In the derivatization step (reaction in Scheme 1), three solutions are mixed together: (i) 300 μL standard solution (hereafter denoted as STD mix) or sample extract in the corresponding solvent, (ii) 400 μL sodium carbonate/bicarbonate buffer ($Na_2CO_3$/$NaHCO_3$), and (iii) 300 μL DnsCl dissolved in acetone. The influence of every mixture component was tested and optimized, as are solvents for standards and sample extraction (MQ, ACN, MeOH, 50% MeOH, 50% ACN, and 80% ACN; all percentages refer to dilution with MQ water), buffer pH (8.9–12.0) and strength (10–500 mM), and concentration of DnsCl (0.1–3 mg mL$^{-1}$). The total volume of the reaction mixture was adapted to approximately 1 mL to fit into HPLC vials, with the corresponding volumes of particular components similar to previously published works (Guo et al., 2011). The reaction mixture was shortly vortexed and incubated on a heated magnetic stirrer with a MonoAluBlock™ (Velp Scientifica) segment for optimal temperature transfer, while the temperature was regulated by a thermometer in a reference vial. Reaction conditions were further tested for different reaction times (5–180 min), temperatures (23–80 °C), and the use of mixing (800 rpm) or non-mixing conditions.



**Scheme 1.** Derivatization reaction of phenols with DnsCl.

After incubation, the vials were cooled down for 5 min and FA was added to lower the pH of the reaction mixture to approximately 3.5–4 quenching the reaction and ensuring compatibility with used HPLC columns. Before injection to HPLC, the final solution was filtered through a PTFE syringe filter (0.22 μm).

During the optimization procedure, STD mix was mostly used as a source of target analytes. Among the targeted phenols, CAT is an exception having two possible reaction sites for Dns labeling. If both sites are dansylated in comparable amounts, the sensitivity is non-acceptably compromised, therefore, CAT labeling was optimized for the doubly dansylated product (CAT-Dns$_2$). For the optimization of DnsCl addition, another experiment was performed with use of an ambient PM sample. The required (stoichiometrically in excess) concentration of DnsCl for the derivatization of target components was determined, bearing in mind possible DnsCl hydrolysis and given that DnsCl also reacts with other basic compounds such as amines and other analytes containing the phenolic moiety (Gray, 1972); however, those are out of scope of this manuscript and were not evaluated. It has been shown, however, that as long as a severalfold excess of DnsCl is used, absolute DnsCl concentration is important for the reaction yield and not its excess (Gray, 1972). Therefore, for this experiment, a winter PM sample was used (collected 29.1. 2016 in Maribor, Slovenia; donated by Slovenian Environment Agency) since higher concentrations of phenolic pollutants are anticipated due to seasonal biomass burning sources and specific meteorological conditions such as temperature inversion. Detailed description of optimization experiments can be found in SI section 2.2. and Table S3.

### 2.5. *HPLC method*

Optimization of the derivatization reaction step was mostly performed on an ultra-high-performance LC (UHPLC)-diode array detection (DAD) system (UltiMate 3000 RS; Thermo Scientific, U.S.A.) in order to also observe unreacted phenols, which is not possible with LC-MS (*vide supra*). An HPLC method for the separation of derivatized and underivatized analytes was first adapted from the literature (Guo and Li, 2009). Different HPLC columns, mobile phases, and mobile phase gradients were tested (see Table S4). The parameters that were fixed are injection volume (10 μL), column temperature (30 °C), and UV/VIS detection wavelengths (275 and 350 nm for unreacted phenols and dansylated products, respectively). The flow rate of 0.3 mL min$^{-1}$ was used in combination with a 3 μm particle size column, whereas at testing smaller particle sizes (*i.e.* 1.6 μm), the flow rate was reduced to 0.2 mL min$^{-1}$.

Special attention was paid to the separation of isobaric interferences relevant for ambient PM (*e.g.* isomeric CRE species, and GUA and methylcatechols, MC), to provide best method specificity. Note also that derivatization of CAT can result in two different products (CAT-Dns and CAT-Dns$_2$) with distinct retention times on a column.

For LC-MS determination, the optimized HPLC method was transferred to a similar UHPLC instrument coupled with a triple quadrupole/linear ion trap mass spectrometer (4000 QTRAP LC-MS/MS System; Applied Biosystems/MDS Sciex, Ontario, Canada). The method was only slightly adapted at this step and is reported in this paper as part of the optimized method parameters (Table 1).

### 2.6. *ESI-MS parameters*

Positive mode ESI proved to be appropriate for the ionization of derivatized phenols. Analytes were detected in the multiple-reaction monitoring mode (MRM), measuring two product ions for every

**Table 1**
Optimal parameters for UHLPC-MS/MS determination of dansylated phenols.

| Optimal HPLC parameters | | | |
|---|---|---|---|
| Column | Luna Omega C18 (2.1 × 150 mm, 1.6 μm), Phenomenex | | |
| Mobile phases | A: 0.1% FA in MQ<br>B: 0.1% FA in MeOH | | |
| Injection volume | 10 μL | | |
| Column temperature | 30 °C | | |
| Flow rate | 0.2 mL min$^{-1}$ | | |
| UV/VIS detection[a] | 275, 350 nm | | |
| Gradient (B) | 0–2 min | 30% | |
| | 2–9 min | 30–75% | |
| | 9–25 min | 75% | |
| | 25–31 min | 75–90% | |
| | 31–40 min | 90% | |
| | 40–45 min | 30% | |
| **Optimal MS parameters** | | | |
| Analyte | MRM transitions[b] | Declustering potential (V) | Collision energy (V) |
| PHE-Dns | 328.1 → 171.2 | 60 | 32 |
| | 328.1 → 313.3 | | 30 |
| GUA-Dns | 358.2 → 171.2 | 65 | 30 |
| | 358.2 → 294.0 | | 20 |
| CRE-Dns[c] | 342.2 → 171.2 | 55 | 35 |
| | 342.2 → 326.9 | | 27 |
| CAT-Dns[d] | 344.2 → 171.2 | 60 | 30 |
| | 344.2 → 156.3 | | 50 |
| CAT-Dns₂ | 577.2 → 170.3 | 70 | 50 |
| | 577.2 → 186.0 | | 50 |

[a] Only used for derivatization reaction optimization and applicable to high-concentration samples.

[b] (+)ESI ionization; *m/z* 171 and 156 originate from Dns fragmentation and are used for quantification, other product ions have smaller intensities and are used for identity confirmation only; acquisition times for all ions were 100 msec.

[c] All CRE-Dns isomers have the same characteristic transitions. Only *o*-CRE is selectively measured based on a distinct retention time.

[d] not in use, because the derivatization reaction was optimized so that majority of CAT molecules got transformed into CAT-Dns₂.

analyte at the time (quantification and identification ions).

For the precursor ions, molecular mass of each analyte was increased by 234 Da for one Dns tag $[M\text{-}Dns + H]^+$ or 467 Da for two Dns tags $[M\text{-}Dns_2{+}H]^+$ in the case of CAT-Dns₂ (Guo et al., 2011). During the optimization, the declustering potential (DP) and collision energies (CE) were determined for every analyte and its selected product ions, respectively. The ion spray voltage was set to 5000 V for all experiments. For quantification, product ions with the highest intensity were determined, which turned out to be ions at *m/z* 171 and 156 Da, both resulting from Dns fragmentation (Chang et al., 2010). Only in some cases, other specific product ions could be found (presumably not originating from Dns fragmentation), which were used for identity confirmation.

### 2.7. Performance evaluation

Performance of the developed method for the determination of trace phenols in environmental samples starting with sample preparation step (dansylation reaction) followed by LC-MS analysis was evaluated by determining the limit-of-detection (LOD), linearity, precision, and robustness for every analyte separately.

For the evaluation of homoscedastic properties, six repetitions of a calibration curve (from 0.05 to 3000 ng mL$^{-1}$ plus the reagent blank; concentrations refer to concentrations in STD mix) for PHE, CAT, GUA, and *o*-CRE and three repetitions for *m*-CRE and *p*-CRE were evaluated. The linearity and homoscedasticity were visually assessed from the plotted linear regression models and the corresponding residual plots. Linearity, later also referred to as a measuring range was further evaluated by a combination of HPLC-DAD and LC-MS measurements, to overcome single detector capabilities.

Limit of blank (LOB, (1)) and LOD, (2) were calculated according to Armbruster and Pry (2008), with coefficients of the tabulated *t*-values corresponding to the number of repetitions at 95% confidence level (*i.e.* 2.015, except for 2.920 in the case of *p*/*m*-CRE) (Desimoni and Brunetti, 2015).

$$LOB = mean_{reagent\ blank} + t\left(SD_{reagent\ blank}\right) \tag{1}$$

$$LOD = LOB + t\left(SD_{low\ concentration\ sample}\right) \tag{2}$$

Reproducibility was assessed by a relative standard deviation (RSD) of repetitions calculated over the whole concentration range and the maximum RSD in the range of expected ambient sample levels was taken as the precision of the method.

Data analysis was performed with use of Chromeleon 7.2 SR4 (Thermo Scientific) and Analyst software, version 1.5 (Applied Biosystems/MSD Analytical Technologies Instruments), and the statistical analysis was performed in program R with included dplyr, lmtest (Zeileis and Hothorn, 2002), and tibble (Müller and Wickham, 2019) packages.

The influence of blanks was also investigated and they were subtracted when necessary. Blanks were prepared for every step of the developed method (reagent and filter blanks; see SI section 2.3), to investigate if impurities from the solvents, reagents, or filter matrix contribute to the signal.

Robustness of the dansylation reaction was tested by comparing different combinations of reaction time (30, 60, 90 min) and temperature (23, 40, 60 °C). The experiment was conducted on two standard mixes (at 0.2 and 200 ng mL$^{-1}$) and one PM sample (collected February 9, 2016 in Maribor; donated by Slovenian Environment Agency), and performed in three replicates. RSD was calculated for every measurement condition to examine in what extent the reaction parameters influence the reaction yield. Stability of dansylated products was further assessed by a repetitive measurement of one standard mix and one sample 14 days after the reaction had been performed. Between the measurements, the samples were stored in a refrigerator and quantification was always made with use of a fresh calibration curve.

For the evaluation of extraction efficiency, blank filters were spiked with a standard mix, since no commercially available certified reference material (CRM) exist for phenols. Equal areas of blank filters as used for sample extraction were spiked with two different standard concentrations (500 and 5000 ng mL$^{-1}$, 20 μL spiking volume) and dried in a refrigerator to reduce analyte evaporation. Four replicates were made for every concentration, except for *m*-CRE and *p*-CRE with only two replicates performed. After the solvent had evaporated, the filters were immediately processed in the same way as PM samples.

### 2.8. Real sample analysis

For quantification, a weighted linear calibration curve incorporated in the Analyst software was used (weighing factor as appropriate for every analyte: $x^{-1}$ or $x^{-2}$), substantially improving fitting in the lower concentration range where the majority of analytes were measured. Blank filter was processed simultaneously with the samples and its signal was subtracted from the sample signals in the case of PHE (blank concentrations for CAT, GUA, *o*-CRE, and *p*/*m*-CRE were below LOD).

## 3. Results and discussion

One parameter at the time was optimized in the course of method development. Optimal instrumental parameters are summarized in Table 1 and described in detail in SI.

### 3.1. Optimal chromatographic separation and detection parameters

All target analytes were successfully separated on the column (Fig. 1,

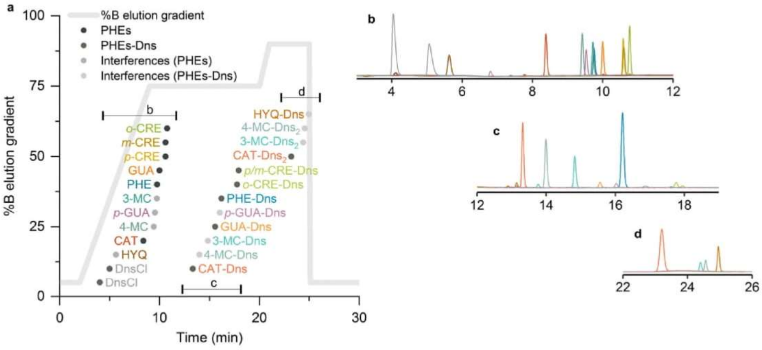


**Fig. 1.** Mobile phase gradient and analyte retention times as measured by HPLC-DAD during the optimization. HPLC chromatograms on the right (gathered in b,c,d) were measured for each analyte separately. Peak heights are not in scale and are only used to present separation efficiency. The two DnsCl peaks are presumably unreacted DnsCl and its hydrolysis product (Dns-OH), however, since their $m/z$ were not confirmed on ESI-MS, both peaks are labeled as DnsCl.

Table S5), except for *p/m*-CRE-Dns, which co-elute at the same retention time, RT. Although we could not achieve separation of p/m-CRE-Dns, their quantification should be possible considering distinct ratios of the $m/z$ 171.2 and 326.9 product ions for the two compounds (approximately 10:1 for *m*-CRE-Dns and 25:1 for *p*-CRE-Dns). However, differentiation is limited by the poor sensitivity of the $m/z$ 326.9 ion and measurement uncertainties. The possibility of p/m-CRE-Dns separation is, therefore, conditioned by their concentration in a sample. On the

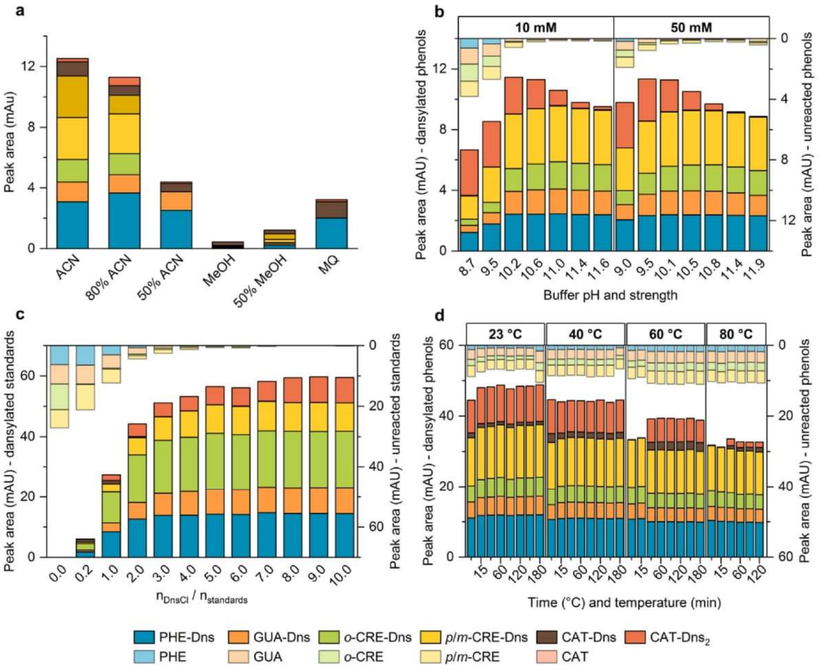


**Fig. 2.** Reaction optimization: **a** solvents, **b** buffer pH and strength, **c** DnsCl concentration, and **d** reaction time (5, 15, 30, 60, 90, 120, 150, and 180 min) and temperature. The stacked columns on the bottom-left axes represent dansylated phenols and on the top-right axes residues of unreacted phenols are shown. Unreacted CAT could not be detected, likely due to poor retention on the column and coelution with solvents. Absorbances at different wavelengths were measured for unreacted and dansylated phenols, therefore their absolute signal intensities cannot be compared. Detailed reaction conditions for all these experiments are found in SI.

other hand, other expected isobaric interferences, such as GUA and MC, were successfully separated on the UHPLC basis.

### 3.2. Dansylation reaction optimization

The following reaction parameters were determined optimally for the group of targeted phenols: 80% ACN in MQ water as a STD mix/ extraction solvent, 50 mM carbonate buffer pH 10.1, 1500 ng mL$^{-1}$ DnsCl considering the applied concentrations and volumes or $n_{DnsCl}/n_{standards} > 3.0$ for any other case, and 40 min reaction at 40 °C under mixing conditions. Detailed description and comments on reaction parameters optimization are found in SI, along with the graphical representation of results for DnsCl amount optimization on ambient PM sample (Fig. S1) and the comparison of mixing and non-mixing conditions (Fig. S2).

The solvent had the highest influence on the measured signal intensity, with ACN performing best and MeOH (Fig. 2a) the worst; similar results were reported for alkylphenols (Pernica et al., 2015). The buffer pH and DnsCl amount (Fig. 2b–c) were optimized with regard to the competitive hydrolysis side reaction, which always consumes a part of DnsCl and thus has to be added in excess (Gray, 1972). The reaction time did not significantly influence the reaction yield (except for CAT) and the signals were the highest at room temperature (23 °C, except for CAT) (Fig. 2d), although the most frequently used reaction conditions in the literature are at elevated temperature (appx. 60 °C) and at 1 h reaction time (Guo and Li, 2009; Guo et al., 2011; Pernica et al., 2015, 2021). However, since it is easier to provide stable reaction conditions at temperatures slightly above room temperature, 40 °C was finally chosen for further analyses.

### 3.3. Method validation

The developed method was evaluated in respect to several validation parameters (Kruve et al., 2015) which are shown in Table 2.

Selectivity and specificity of determination were achieved by separation of the analytes on an HPLC column and measurement of specific mass to charge ratios (*m/z* value), together with characteristic product ions for the target phenolic compounds (MS/MS determination). The only identified interferences are thus *p*-CRE and *m*-CRE, since they exhibit the same MRM transitions and also elute at the same retention time. For this reason, *p*-CRE and *m*-CRE are detected together and 10% underestimation is estimated if a sample contains only *m*-CRE and is calibrated by *p*-CRE (and *vice versa*). Although *p*- and *m*-CRE-Dns show different ratios of *m/z* 171.2 and 326.9 product ions (*vide supra*), concentrations of *p*- and *m*-CRE in PM samples are mostly too low to allow for their separation on this basis.

Overall, the method exhibits good precision for all analyte standards (RSD below 7%, except for CAT below 18%, dependent on concentration), and the test PM sample (below 5% for GUA, *o*-CRE, and *p*/*m*-CRE; PHE and CAT were not detected). Refer here to Table 2.

Linearity was examined at two different levels: for the dansylation reaction and for the analyte detection by LC-MS. For the LC-MS analysis, linearity was confirmed below approximately 100 ng mL$^{-1}$. Note, however, that the upper limit concentration is not problematic for the application, because the observed concentrations in ambient PM samples are very low (below 5 ng mL$^{-1}$, except for CAT around 100 ng mL$^{-1}$ in one single sample). For the lower concentration limits, see LODs in Table 2. Nevertheless, combining the lower measurement range of LC-MS (roughly 0.05–100 ng mL$^{-1}$) with the higher measurement range of HPLC-DAD (roughly 50–5000 ng mL$^{-1}$), we were able to achieve linearity over a wide concentration range investigated (below 0.06–5000 ng mL$^{-1}$ for all analytes, except CAT-Dns$_2$ 0.2–5000 ng mL$^{-1}$).

In order to qualify for simple linear fits linear models should further meet the condition of homogeneously distributed residuals. Our calibration curves, however, showed heteroscedastic characteristics, *i.e.* the variance was increasing with concentration. Therefore, different weights (*e.g.* x$^{-1}$, x$^{-2}$) and transformations (*e.g.* log(y) and log(x)) were applied to find the most appropriate calibration model. The best correction was achieved with log(y) and log(x) transformations (Fig. S3), however, a weighted linear model build in Analyst software was also found adequate for real-sample analysis (*vide infra*). All calibration curves exhibited statistically significant relationship between variables (p-values $< 0.05$), with good fitting to the observed data set ($R^2 > 0.99$).

The derivatization step proved robust, given that small differences in the reaction time and temperature did not lead to higher uncertainty (RSD between repetitions of different combinations of reaction time and temperature was below 5%, except for CAT 7% at 200 ng mL$^{-1}$). Moreover, the dansylated products are stable if refrigerated for at least 14 days (longer time periods were not tested).

For ambient PM sample quantification, impurities in filter blanks may also interfere with the measurement and should be carefully considered. In our case, blank filters contained PHE interference, which had to be subtracted from the sample signals (see the next section).

### 3.4. Method application

The developed method was applied to 12 ambient PM$_{2.5}$ samples from Ljubljana (7 winter and 5 spring samples, see Table S2). Extraction efficiency determined by spiking blank filters with liquid compound standards were 50–70% (see Table 2), and the concentrations determined in PM samples were corrected accordingly. Although we did not opt for extraction optimization (*e.g.* multiple extraction steps or higher solvent volumes and subsequent evaporation could do better), we

**Table 2**
Parameters characterizing method performance.

| Analyte | LOD for LC-MS (ng mL$^{-1}$)[a] | LOD for HPLC-DAD (ng mL$^{-1}$)[a] | Extraction efficiency (%) | Linearity[b] (ng mL$^{-1}$) | Precision[c] (%) | Product stability | Measuring range[d] (ng mL$^{-1}$) | Interferences[e] |
|---|---|---|---|---|---|---|---|---|
| PH-Dns | 0.05 | 41 | 60 | LOD–100 | 5 | >14 days | 0.05–5000 | unknown |
| GUA-Dns | 0.05 | 60 | 55 | LOD–100 | 7 | >14 days | 0.05–5000 | unknown |
| *o*-CRE-Dns | 0.06 | 80 | 70 | LOD–100 | 7 | >14 days | 0.06–5000 | unknown |
| *p*-CRE-Dns | 0.05 | 44[f] | 50 | LOD–100 | 5 | >14 days | 0.05–5000 | *m*-CRE |
| *m*-CRE-Dns | 0.03 | 44[f] | 50 | LOD–100 | 4 | >14 days | 0.03–5000 | *p*-CRE |
| CAT-Dns$_2$ | 0.2 | 60 | 60 | LOD–100 | 18 | >14 days | 0.2–5000 | unknown |

[a] Absolute concentration in the final solution.
[b] Linear range of LC-MS calibration curve.
[c] maximal RSD measured in the LC-MS range. At higher concentrations, RSDs were typically 4–25 times lower.
[d] measurement range (LC-MS and HPLC-DAD together).
[e] Only interferences at the same RT are listed; interferences solved by separation on the column are not included.
[f] *m*- and *p*-CRE-Dns determined together in one peak, as a sum of *p*- and *m*-CRE-Dns.

attribute moderate analyte recoveries to the volatile nature of the studied phenols (analytes could be lost *e.g.* already during drying of the spiked filter, which would only escalate during solvent evaporation, if applied). Special care was thus also given to sample handling and storage. We kept the samples in a freezer and after defrosting, they were analyzed as soon as possible.

At this point it is worth nothing that due to semi-volatile characteristics of the targeted analytes, sampling procedure is also very important. At certain conditions in time (*e.g.* temperature, analyte concentrations), semi-volatile compounds are in balance between particulate and gas phases; however, during 24 h sampling the conditions and the balance vary, which can result in desorption or absorption of the analytes from/on the PM already collected on a filter. The standard EN12341 specifies the recommended flow rate and temperature limitations to minimize the loss of semi-volatiles, which are then considered zero by convention (EN12341:2014). However, when planning air sampling campaigns, where semi-volatiles are of interest, it might be worth considering to adjust sampling start/end time to sunrise, when the temperatures and consequently evaporation of analytes are the lowest. When using sequential PM sampler, interday temperature variability can also cause loss of analytes from the sampled filters, therefore, after sampling, filters should be stored in a cooled compartment as described in detail in EN12341.

The majority of analytes in spring samples were below LOD ($PM_{2.5}$ masses were also low, mostly below 10 μg $m^{-3}$), except for one spring sample where we detected *p/m*-CRE, which might be the result of increased automobile exhaust from a local construction site. As expected, winter samples with higher $PM_{2.5}$ masses (above 20 μg $m^{-3}$ in days with average daily temperature close to or below 0 °C) also exhibited higher/detectable concentrations of phenols (Fig. 3 and Fig. S4). The only sample in which all target analytes could be quantified was the one with the highest PM mass (80 μg $m^{-3}$) and the lowest average daily temperature (−3.9 °C), which seems reasonable due to increased biomass burning for heating purposes.

Among the measured analytes, CAT concentrations were the highest, corresponding to its lowest volatility and highest water-solubility (Pubchem, National Library of Medicine). Low concentrations of GUA were detected in a majority of winter samples, whereas PHE and CRE were above LOD in only a few. *o*-CRE was detected in one single PM sample (the one with the highest PM mass, though), while *p/m*-CRE were above LOD in several samples, probably due to their cumulative determination in a single chromatographic peak. As already mentioned, we were unable to distinguish between *m*-CRE and *p*-CRE in the samples, because their concentrations were too low to be determined on the basis of their fragmentation patterns.

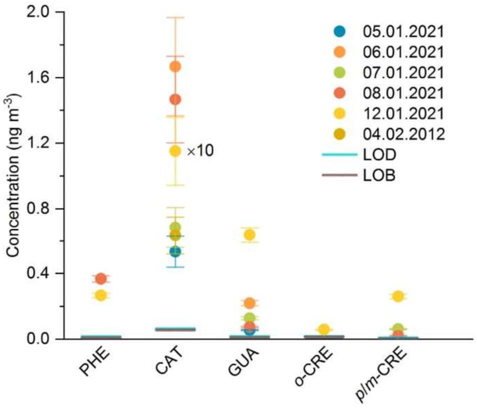


**Fig. 3.** Concentrations of phenols in urban PM2.5 samples. The dots represent different samples named after the date of sampling. Only winter PM samples which exhibited values above LOD are presented. In the case of *p/m*-CRE, LOD and LOB of *m*-CRE are considered (*p*-CRE has higher limits; see Table S2). The results for CAT without EDTA addition are shown.

In the atmosphere, simple phenols can act as precursors to secondary organic aerosols and their nitrated analogues are known SOA tracers (Iinuma et al., 2010; Finewax et al., 2018; Wang et al., 2019). According to the literature data for the same sampling site (Ljubljana), nitrated phenols show a similar pattern of analyte distribution to our targeted phenols (Kitanovski et al., 2012; Frka et al., 2022). High concentrations of nitrated phenols are typically observed in winter PM samples (10- to a few 100-times higher than in summer), correlating well with increased biomass burning emissions. The highest concentrations have been observed for 4-nitrocatechol, which corresponds to the highest measured concentrations of CAT in this work and implies a possible precursor-product relationship, which needs to be further investigated. Nitrophenol and nitroguaiacol concentrations were a few-times lower than those of nitrocatechols (in some winter samples even below LOD), similar to the results for PHE and GUA in our study. Methylnitrocatechols again followed the winter-summer trend of their tentative precursor CRE, however, some methylnitrocatechol concentrations were extremely high, even close to the level of nitrocatechol, which could imply that nitration of CREs is not the only source of methylnitrocatechols in the atmosphere. Overall, the measured concentrations of precursor phenols were a few times lower than their secondary nitrated analogues (except for GUA exhibiting similar concentrations to nitroguaiacols in the samples), which indicates rapid nitration reactions in the atmosphere, higher volatility of precursor phenols and/or better stability of SOA markers and their longer persistence in the atmosphere.

Furthermore, PM samples contain a mix of various components, including metals (Ogrizek et al., 2021, 2022). It is known that catechols form metal complexes in aqueous solutions (Xu, 2013), which could hinder the dansylation reaction (Miyano et al., 1985). These complexes can be reversed by the addition of a stronger metal-chelating agent compared to catechols, *e.g.* ethylenediaminetetraacetic acid (EDTA). However, in this case, special caution should be put to the addition of DnsCl, since EDTA also consumes a part of the reagent (Miyano et al., 1985). With the addition of 409 μM EDTA in the extraction solvent and a double amount of DnsCl we measured 2-times larger CAT concentrations in the same samples, while other analyte signals (PHE, GUA, CRE) were not affected by EDTA addition.

### 3.5. Conclusions

In this study, we present an analytical method for the determination of simple phenols in ambient PM by LC-MS with prior derivatization with DnsCl. Instrumental parameters and reaction conditions, including the concentration of derivatization agent were optimized to obtain the best sensitivity and precision for trace detection of PHE, CAT, GUA, and CREs in environmental samples, which was assessed through partial method validation. The developed method is specific and selective (only minimal interferences were identified), robust, and forms stable analytes, for at least two weeks. Linear response is shown over the desired concentration range, with heteroscedastic characteristics that were addressed by applying a weighted linear regression. High precision and very low LODs were obtained for all dansylated analytes; however, in spring PM samples, for which biomass burning is not typical (in contrast to winter), concentrations of target phenols were mostly too low to be determined.

In contrast to their substituted analogues, such as nitrophenols and aromatic carboxylic acids, simple phenols have not been measured in PM samples until now because of sensitivity limitations. One could argue that simple phenols are volatile and thus predominantly distributed in the atmospheric gaseous phase; however, their abundance (even if low) and correlation with the related secondary products (*e.g.* nitrophenols) could shed light on secondary organic aerosol formation pathways, which is made possible with the method developed in this study. The targeted phenols, however, are not the only analytes in PM that react with DnsCl. Some unknown peaks with the same MRM transitions to GUA were detected in most PM samples. Possible candidates for those unknown peaks are methyl-catechols, but their RT have not been confirmed.

It should be noted at this point that the amount of derivatization reagent cannot be simply adjusted for more or less concentrated samples. Namely, ensuring a stable pH, hydrolysis becomes a pseudo-first order reaction (note the concentration of $OH^-$ is constant), which is in competition with the second-order labelling reactions. During the experiment, as the concentration of reactants (but $OH^-$) is reduced, the rate of second-order rate reactions drops down faster compared with the pseudo-first order side reaction, favoring hydrolysis. A similar behavior, however, is expected at low-concentration samples. Therefore, we optimized the method for samples with high concentration and even if one expects lower concentrations of phenols in a sample than used during optimization, it is not appropriate to significantly reduce DnsCl concentration in the reaction mixture. In the lower concentration regime, the labelling reaction will be slower, whereas hydrolysis reaction rate will not change comparably. Consequently, proportionally more DnsCl will undergo hydrolysis and a greater excess will be needed in order to complete derivatization. To overcome this, the same amount of DnsCl is suggested for low- and high-concentration samples, so that a larger excess of DnsCl is automatically achieved in case of lower analyte concentrations. For samples from strongly polluted environments, however, we suggest the amount of DnsCl be confirmed sufficient.

We show in this paper that although simple phenols are considered relatively volatile, they can be found in atmospheric particulate phase, especially in colder seasons and in areas affected by biomass burning emissions. There, they could act as precursors to aqueous-phase secondary organic aerosols, which needs to be confirmed with simultaneous determination of precursor and nitrated phenols in seasonal PM samples. Moreover, PHE is often contained in polluted wastewater from industrial, agricultural and domestic activities; although the developed method is optimized for PM, it could also be used for other environmental samples, with slight modification in respect to sample preparation and concentration levels.

## Authors contributions

**Monika Ogrizek**: Investigation, Formal analysis, Writing – original draft, Visualization. **Ana Kroflič**; : Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition. **Martin Šala**: Conceptualization, Methodology, Writing – original draft, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.135313.

## References

Armbruster, D.A., Pry, T., 2008. Limit of blank, limit of detection and limit of quantitation. Clin. Biochem. Rev. 29 (Suppl. 1), S49–S52.

Borhan, M.S., Capareda, S., Mukhtar, S., Faulkner, W.B., McGee, R., Parnell, C.B., 2012. Comparison of seasonal phenol and p-cresol emissions from ground-level area sources in a dairy operation in central Texas. J. Air Waste Manage. Assoc. 62, 381–392.

Campen, M., Robertson, S., Lund, A., Lucero, J., McDonald, J., 2014. Engine exhaust particulate and gas phase contributions to vascular toxicity. Inhal. Toxicol. 26, 353–360.

Chang, H., Wan, Y., Naile, J., Zhang, X.W., Wiseman, S., Hecker, M., Lam, M.H.W., Giesy, J.P., Jones, P.D., 2010. Simultaneous quantification of multiple classes of phenolic compounds in blood plasma by liquid chromatography-electrospray tandem mass spectrometry. J. Chromatogr. A 1217, 506–513.

Chen, Y.T., Huang, H.C., Hsieh, Y.J., Fu, S.H., Li, L., Chen, C.L., Chu, L.J., Yu, J.S., 2019. Targeting amine- and phenol-containing metabolites in urine by dansylation isotope labeling and liquid chromatography mass spectrometry for evaluation of bladder cancer biomarkers. J. Food Drug Anal. 27, 460–474.

Desimoni, E., Brunetti, B., 2015. About estimating the limit of detection by the signal to noise approach. Pharm. Anal. Acta 6.

Fan, H., Papouskova, B., Lemr, K., Wigginton, J.G., Schug, K.A., 2014. Bulk derivatization and direct injection of human cerebrospinal fluid for trace-level quantification of endogenous estrogens using trap-and-elute liquid chromatography with tandem mass spectrometry. J. Separ. Sci. 37, 2010–2017.

Feng-Yang, B., Zi-Yu, L., Shuang, N., Yong-Sheng, Y., Zhou, Y., Guang-Hui, W., Zhen, Z., Xiu-Mei, P., 2022. Metal-free catalysis for the reaction of nitrogen dioxide dimer with phenol: an unexpected favorable source of nitrate and aerosol precursors in vehicle exhaust. Chemosphere 291, 132705.

Ferreira, M.S., Arruda, A.M.M., Pepi, G.T., Martho, A.C., Maximiano, P.M., Ricci, L., Riccio, M.F., Noboli, A.C., Serafim, P., 2017. High sensitivity method validated to quantify estradiol in human plasma by LC-MS/MS. J. Chromatogr. B 1064, 109–114.

Finewax, Z., de Gouw, J.A., Ziemann, P.J., 2018. Identification and quantification of 4-nitrocatechol formed from OH and NO3 radical-initiated reactions of catechol in air in the presence of NOx: implications for secondary organic aerosol formation from biomass burning. Environ. Sci. Technol. 52, 1981–1989.

Forbes, P., 2020. Atmospheric chemistry analysis: a review. Anal. Chem. 92, 455–472.

Frka, S., Šala, M., Brodnik, H., Štefane, B., Kroflič, A., Grgić, I., 2022. Seasonal variability of nitroaromatic compounds in ambient aerosols: mass size distribution, possible sources and contribution to water-soluble brown carbon light absorption. Chemosphere 299, 134381.

Frka, S., Šala, M., Kroflič, A., Huš, M., Čusak, A., Grgić, I., 2016. Quantum chemical calculations resolved identification of methylnitrocatechols in atmospheric aerosols. Environ. Sci. Technol. 50, 5526–5535.

Gray, W.R., 1972. 8 End-group analysis using dansyl chloride. Methods Enzymol. 25, 121–138.

Guo, K., Bamforth, F., Li, L.A., 2011. Qualitative metabolome analysis of human cerebrospinal fluid by C-13-/C-12-isotope dansylation labeling combined with liquid chromatography fourier transform ion cyclotron resonance mass spectrometry. J. Am. Soc. Mass Spectrom. 22, 339–347.

Guo, K., Li, L., 2009. Differential C-12/C-13-isotope dansylation labeling and fast liquid chromatography/mass spectrometry for absolute and relative quantification of the metabolome. Anal. Chem. 81, 3919–3932.

Hawthorne, S.B., Krieger, M.S., Miller, D.J., Mathiason, M.B., 1989. Collection and quantitation of methoxylated phenol tracers for atmospheric-pollution from residential wood stoves. Environ. Sci. Technol. 23, 470–475.

He, L., Schaefer, T., Otto, T., Kroflic, A., Herrmann, H., 2019. Kinetic and theoretical study of the atmospheric aqueous-phase reactions of OH radicals with methoxyphenolic compounds. J. Phys. Chem. A 123, 7828–7838.

Hoffmann, D., Iinuma, Y., Herrmann, H., 2007. Development of a method for fast analysis of phenolic molecular markers in biomass burning particles using high performance liquid chromatography/atmo spheric pressure chemical ionisation mass spectrometry. J. Chromatogr. A 1143, 168–175.

Iinuma, Y., Boge, O., Grafe, R., Herrmann, H., 2010. Methyl-nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols. Environ. Sci. Technol. 44, 8453–8459.

Jakovljević, I., Simić, I., Mendaš, G., Štrukil, Z.S., Žužul, S., Gluščić, V., Godec, R., Pehnec, G., Bešlić, I., Milinković, A., Alempijević, S.B., Šala, M., Ogrizek, M., Frka, S., 2021. Pollution levels and deposition processes of airborne organic pollutants over the central Adriatic area: temporal variabilities and source identification. Mar. Pollut. Bull. 172, 18.

Jaoui, M., Lewandowski, M., Offenberg, J.H., Colon, M., Docherty, K.S., Kleindienst, T.E., 2018. Characterization of aerosol nitroaromatic compounds: validation of an experimental method. J. Mass Spectrom. 53, 680–692.

Kitanovski, Z., Grgić, I., Vermeylen, R., Claeys, M., Maenhaut, W., 2012. Liquid chromatography tandem mass spectrometry method for characterization of monoaromatic nitro-compounds in atmospheric particulate matter. J. Chromatogr. A 1268, 35–43.

Kroflič, A., Anders, J., Drventić, I., Mettke, P., Böge, O., Mutzel, A., Kleffmann, J., Herrmann, H., 2021. Guaiacol nitration in a simulated atmospheric aerosol with an emphasis on atmospheric nitrophenol formation mechanisms. ACS Earth Space Chem 5, 1083–1093.

Kruve, A., Rebane, R., Kipper, K., Oldekop, M.L., Evard, H., Herodes, K., Ravio, P., Leito, I., 2015. Tutorial review on validation of liquid chromatography-mass spectrometry methods: Part I. Anal. Chim. Acta 870, 29–44.

Liang, Y.H., Wang, X.F., Dong, S.W., Liu, Z.Y., Mu, J.S., Lu, C.Y., Zhang, J., Li, M., Xue, L. K., Wang, W.X., 2020. Size distributions of nitrated phenols in winter at a coastal site in north China and the impacts from primary sources and secondary formation. Chemosphere 250, 9.

Luo, X., Li, L., 2017. Metabolomics of small numbers of cells: metabolomic profiling of 100, 1000, and 10000 human breast cancer cells. Anal. Chem. 89, 11664–11671.

Miyano, H., Toyooka, T., Imai, K., Nakajima, T., 1985. Influences of metal-ions on the reaction of amino and imino acids with fluorogenic reagents. Anal. Biochem. 150, 125–130.

Moldoveanu, S.C., Kiser, M., 2007. Gas chromatography/mass spectrometry versus liquid chromatography/fluorescence detection in the analysis of phenols in mainstream cigarette smoke. J. Chromatogr. A 1141, 90–97.

Morville, S., Scheyer, A., Mirabel, P., Millet, M., 2004. A multiresidue method for the analysis of phenols and nitrophenols in the atmosphere. J. Environ. Monit. 6, 963–966.

Müller, K., Wickham, H., 2019. Tibble: Simple Data Frames, R Package, version 2.0.1.

Mung, D., Li, L., 2017. Development of chemical isotope labeling LC-MS for milk metabolomics: comprehensive and quantitative profiling of the amine/phenol submetabolome. Anal. Chem. 89, 4435–4443.

Ogrizek, M., Jaćimović, R., Šala, M., Kroflič, A., 2021. No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters. Talanta 226, 10.

Ogrizek, M., Kroflič, A., Šala, M., 2022. Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter. Trends Environ. Anal. Chem. 33, e00155.

Pernica, M., Lesniaková, R., Doležalová, D., Šimek, Z., 2021. Analysis of alkylphenols and bisphenols in soils using liquid chromatography-tandem mass spectrometry. Int. J. Environ. Anal. Chem. 101, 1287–1301.

Pernica, M., Poloucká, P., Seifertová, M., Šimek, Z., 2015. Determination of alkylphenols in water samples using liquid chromatography-tandem mass spectrometry after pre-column derivatization with dansyl chloride. J. Chromatogr. A 1417, 49–56.

Pillar, E.A., Guzman, M.I., 2017. Oxidation of substituted catechols at the air-water interface: production of carboxylic acids, quinones, and polyphenols. Environ. Sci. Technol. 51, 4951–4959.

Pistonesi, M.F., Di Nezio, M.S., Centurion, M.E., Lista, A.G., Fragoso, W.D., Pontes, M.J. C., Araujo, M.C.U., Band, B.S.F., 2010. Simultaneous determination of hydroquinone, resorcinol, phenol, m-cresol and p-cresol in untreated air samples using spectrofluorimetry and a custom multiple linear regression-successive projection algorithm. Talanta 83, 320–323.

Risner, C.H., Cash, S.L., 1990. A high-performance liquid-chromatographic determination of major phenolic-compounds in tobacco-smoke. J. Chromatogr. Sci. 28, 239–244.

Sturaro, A., Rella, R., Parvoli, G., Ferrara, D., 2010. Long-term phenol, cresols and BTEX monitoring in urban air. Environ. Monit. Assess. 164, 93–100.

Wang, Y., Hu, M., Wang, Y., Zheng, J., Shang, D., Yang, Y., Liu, Y., Li, X., Tang, R., Zhu, W., Du, Z., Wu, Y., Guo, S., Wu, Z., Lou, S., Hallquist, M., Yu, J.Z., 2019. The formation of nitro-aromatic compounds under high NOx and anthropogenic VOC conditions in urban Beijing, China. Atmos. Chem. Phys. 19, 7649–7665.

Wang, Z.H., Yu, J., Yao, J.X., Wu, L.L., Xiao, H., Wang, J., Gao, R., 2018. Simultaneous identification and quantification of bisphenol A and 12 bisphenol analogues in environmental samples using precolumn derivatization and ultra high performance liquid chromatography with tandem mass spectrometry. J. Separ. Sci. 41, 2269–2278.

Xu, W.X., Hu, Y.F., Wu, M.H., Miao, E.M., Zhou, H., Zhang, X.W., Zhan, J.J., 2021. Determination of phenolic compounds in estuary water and sediment by solid-phase isotope dansylation coupled with liquid chromatography-high resolution mass spectrometry. Anal. Methods 13, 1404–1411.

Xu, Z.P., 2013. Mechanics of metal-catecholate complexes: the roles of coordination state and metal types. Sci. Rep. 3, 7.

Yang, S.H., Morgan, A.A., Nguyen, H.P., Moore, H., Figard, B.J., Schug, K.A., 2011. Quantitative determination of bisphenol a from human saliva using bulk derivatization and trap-and-elute liquid chromatography coupled to electrospray ionization mass spectrometry. Environ. Toxicol. Chem. 30, 1243–1251.

Yao, J.X., Wang, J., Wu, L.L., Lu, H.H., Wang, Z.H., Yu, P.F., Xiao, H., Gao, R., Yu, J., 2020. Perinatal exposure to bisphenol A causes a disturbance of neurotransmitter metabolic pathways in female mouse offspring: a focus on the tryptophan and dopamine pathways. Chemosphere 254, 11.

Zeileis, A., Hothorn, T., 2002. Diagnostic checking in regression relationships. R. News 2, 7–10.

Zhao, S., Luo, X., Li, L., 2016. Chemical isotope labeling LC-MS for high coverage and quantitative profiling of the hydroxyl submetabolome in metabolomics. Anal. Chem. 88, 10617–10623.

# Chapter 4

# Conclusions

The presented dissertation contributes to the scientific field by providing two new methods for better characterization of atmospheric PM, which is most commonly collected on the universal quartz fiber filters. The first method for the characterization of elemental composition by the direct analysis of PM captured on a filter with LA-ICPMS was developed as a better alternative to the current standard MW/ICPMS method, providing more accurate determination of more elements without producing any toxic waste and burdening the environment. The second method for the determination of phenolic compounds by LC-MS with previous derivatization with DnsCl was intended for studying phenolic composition of ambient PM and further the mechanisms of their transformations in the atmosphere. By evaluating the method performance and by their application to real-life PM samples, we demonstrated that they are consistent with good analytical practices and can be applied for the intended purposes and even wider.

The goal of the dissertation was summed up in six hypotheses, which were addressed in the four presented articles and one manuscript. The first four hypotheses assumed the possibility of PM elemental determination with LA-ICPMS and the last two hypotheses referred to the analysis of particulate simple phenols by LC-MS/MS.

The **first hypothesis** assumes the feasibility of accurate determination of the elemental composition of PM collected on quartz fiber filters (*i.e.* PM samples) by LA-ICPMS. The method was developed and presented in Article 2. The method exhibits good performance in terms of accuracy, low LOD, and multi-element determination of at least 20 elements at a time. Additionally, in the paper, the generally accepted "homogeneity" of PM samples was questioned and the sufficient size of a sample needed for accurate LA-ICPMS analysis was statistically determined (*i.e.* $3 \times 12$ mm$^2$). Smaller sizes did not provide results representative of the whole PM sample. The calibration of LA-ICPMS measurements is often difficult, so even in our case it did pose some challenges, since matrix-matched standard for the elemental composition on quartz fiber filter is not commercially available, and the one intended for OC/EC determination (*i.e.* NIST RM 8785) was found inappropriate. An alternative approach of exploiting $k_0$-INAA for the standard production turned out suitable for the calibration purpose, however, it is not practical when it comes to regular air-quality monitoring. The absolute method $k_0$-INAA was also used for testing the accuracy of the developed LA-ICPMS method, where no statistical difference between the methods was observed for all the compared elements. Therefore, based on the resulting good analytical performance of the developed LA-ICPMS method, I can confirm the first hypothesis.

In the **second hypothesis,** performance of LA-ICPMS compared to the standard MW/ICPMS method was questioned, as well as its potential to replace the standard method in air-quality monitoring activities in the future. These questions were addressed in Articles 1 and 2. In the second paper, the same ambient samples were analyzed with three different methods (developed LA-ICPMS, standardized MW/ICPMS, and absolute $k_0$-INAA). The results of comparison show higher agreement of LA-ICPMS with the absolute method $k_0$-INAA than of MW/ICPMS with $k_0$-INAA, which points to the higher accuracy of LA-ICPMS and insufficient digestion efficiency in the case of the standard method for some elements. Based on this experiment, I can confirm the first part of the second hypothesis, stating that the performance of LA-ICPMS is comparable or even better than that of the standardized MW/ICPMS method. The second part of the hypothesis on the potential of LA-ICPMS to become a standard method in the future was critically assessed in the first article. This review paper summarizes the analytical background of the elemental determination of PM and presents drawbacks of the established standard method from different perspectives. State-of-the-art alternative methods most commonly used in atmospheric chemistry research were identified and carefully examined through detailed literature research for their potential to replace the current standard method. One important aspect of assessing alternative methods was the capability of analyzing PM collected on a fiber-based material, as the uneven surface can be a challenge for surface-based techniques. From this aspect, LA-ICPMS turned out as the most promising technique, confirming also the second part of the second hypothesis, because it was recognized as the only green, multi-element, and accurate method capable of analyzing PM directly from the most widely-used quartz fiber filters.

Even though LA-ICPMS was proven better than the established standard method, monitoring agencies typically do not possess LA systems. The 193 nm LA system used for method development in the second article is quite a substantial initial investment, therefore, the possibility of a more affordable LA system would definitely ease the transition to this greener analytical technique and assure wider use of the method. One option of the more affordable LA system is a solid state laser with a 213 nm wavelength. For this reason, the **third hypothesis** assumes that elemental determination is feasible also with a more affordable 213 nm LA system. This hypothesis was addressed in Manuscript 3, where the developed LA-ICPMS method was adapted and optimized for the 213 nm LA system. After we had demonstrated that PM samples can be successfully analyzed by the alternative LA system with use of the new set of optimal instrument parameters, the accuracy of the measurement was further assessed by comparison with the 193 nm LA system and the standard MW/ICPMS method. The comparison of all three methods did not show any statistical differences, confirming that the determination with 213 nm LA system is as accurate as the other two tested methods. Still, the 193 nm LA system had some benefits in terms of lower LOD and higher sensitivity for some elements (*e.g.* Ba, Cd, Pb, Sb, Sn, and Tl), but generally, 213 nm LA was proven suitable for the monitoring purposes since it meets the criteria for limit values, LODs and measurement ranges in the relevant EU Directives. Therefore, I can conclude that 213 nm LA-ICPMS is a green, multi-element method that could replace the standard method in the future, and due to its affordability it will ease the transition to green analytical methods in air-quality monitoring sector. According to these findings, I can confirm the third hypothesis.

After the LA-ICPMS method had been developed, we applied it in a research project on ambient $PM_{2.5}$ samples collected on quartz fiber filters in field campaigns conducted in Ljubljana in different seasons over a year. Within this project, the robustness of the LA-ICPMS method was challenged. A large number of samples with different PM concentrations and compositions that varied among the seasons due to different pollution sources, including variable content of trace elements, was analyzed, which brings us to the fourth hypothesis.

The **fourth hypothesis** targets the application of the developed LA-ICPMS method and assumes the concentration of anthropogenic pollutants is higher in winter due to heating purposes and/or specific meteorological conditions. Seasonal trends of airborne trace elements in Ljubljana were investigated in Article 4, together with the performed source apportionment study. Typical anthropogenically released trace elements (*e.g.* As, Cd, Cr, Mn, Mo, Pb, Rb, and Zn) were found in significantly higher concentrations in autumn and winter, when the consumption of fossil fuels is typically higher and also because of unfavorable meteorological conditions (*i.e.* calmer atmosphere and temperature inversion events) compared to spring and summer. This investigation gave us enough evidence, therefore I can confirm the fourth hypothesis. Additionally, two special events were also identified in February and June 2021, where elevated concentrations of mostly crustal elements (*e.g.* Al, As, Co, Fe, Mn, Rb, V, K, Mg, Na, and Tl) coincided well with the long-range transport of Saharan dust observed by other monitoring agencies.

With the fourth hypothesis and Article 4 we concluded the research set out to the investigation of the elemental composition of PM by LA-ICPMS. All four hypotheses connected with these research endeavors were confirmed and I can conclude that by demonstrating the usefulness and versatility of the developed method, the objectives set at the beginning of my PhD work were successfully achieved. The only deficiencies still missing are beyond the scope of this research and are more of an engineering task, *i.e.* the buildup of a specialized autosampler, and of producers of reference materials, who need to provide matrix-matched standards available for purchase to a wider community. Beside the elemental content, the organic fraction of PM is equally important and was targeted in the following two hypotheses.

In this aspect, the **fifth hypothesis** assumes that there is a way to extract simple phenols from atmospheric PM and analyze them with LC-MS/MS without any sample pre-concentration step. Therefore, a new method for simple phenols with previous derivatization with DnsCl was developed and is described in Article 5. The newly developed method is able to detect simple phenols in PM samples with use of derivatization reaction, which improves ionization efficiency of the analytes in an ESI source and substantially improves their LODs, neglecting the need for a pre-concentration step. The method exhibits very good performance with good precision, low LODs, sufficient linearity range, minimal interferences (only *p*- and *m*-cresol coeluted), high dansylation reaction reproducibility and long analyte stability, while the extraction efficiency was also shown adequate. With this we can also confirm the fifth hypothesis.

The application of the developed LC-MS/MS method to ambient PM samples was required to test the last, **sixth hypothesis**, which assumes that concentrations of simple phenols are higher during biomass burning seasons compared to warmer months, which was also addressed in Article 5. Analyzed ambient PM samples from different seasons revealed the levels of simple phenols in PM from Ljubljana, and their seasonal trends. The highest concentrations were observed in winter, as it was predicted in the sixth hypothesis, due to the prevalence of their major emission source in this season, which is biomass burning. The highest concentration was measured for catechol, whose determination could be biased due to the formation of complexes with divalent metals present in the PM. However, EDTA added in the extraction solution reversed the formation of complexes and enabled its accurate determination. Phenol and guaiacol were also detected in PM samples, whereas *p*-/*m*-cresol were only found in very low concentrations, and *o*-cresol was mostly below LOD. In the spring period samples, simple phenols were not detected at all, probably because biomass burning is very limited at that time in Ljubljana and the higher temperatures also favor partitioning of semi-volatiles to the gas. With the help of these observations we can also confirm the final, sixth hypothesis.

By the detailed exploration of method performance and its application to ambient PM samples, both hypotheses concerning the determination of simple phenols in PM by LC-MS/MS were also confirmed, providing an analytical method which is easily accessible to the wider atmospheric community.

Looking at the big picture, the development of new methods is only a part of the story and we are only at the beginning stage of investigations, in which the new methods will be applied producing new knowledge in the field of atmospheric chemistry research and wider. LC-MS is a common instrument found in most analytical laboratories since it is widely applicable to the detection of different organic analytes, including in complex matrices, which means that many atmospheric aerosol research groups can now include simple phenols in their research and facilitate achieving our common goal of identifying most problematic air pollutants and limiting their pollution. On the other hand, LA-ICPMS is not such a widespread technique and it might take a longer time for its implementation in the community and for air-quality monitoring purposes. Nevertheless, we are confident that both methods will find their place in the atmospheric chemistry community.

# Appendices

## A.1 Pollution Levels and Deposition Processes of Airborne Organic Pollutants over the Central Adriatic Area: Temporal Variabilities and Source Identification

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https://doi.org/10.1016/j.marpolbul.2021.112873

During the PhD I coauthored a paper published in Marine Pollution Bulletin, where we investigated pollution levels of organic components in ambient PM and PM deposits over the central Adriatic area. The project included a sampling campaign, where the samples of ambient PM, bulk deposits, and wet deposits were collected. The campaign was placed at the costal Adriatic area and lasted for 6 months. Chemical characterization of samples for PAHs, nitroaromatic compounds (NACs), and polychlorinated bisphenyls (PCBs) was performed off-line, where I contributed with the determination of NACs in all three sample types. As a result, the major land and marine traffic emission sources were identified due to diesel and gasoline combustion, which were the major sources of PAHs, whereas biomass burning episodes were strongly connected with the presence of NACs in the samples.

Cooperation in this project was a great opportunity to get acquainted with the determination of NACs, which would be used in a future project. To further explore the topic, beyond the scope of this dissertation, we are planning to perform a larger campaign to investigate the phenolic composition of ambient PM samples, where simple phenols would be treated as precursors and NACs as their secondary compounds. We hope to find seasonal trends and a possible precursor-secondary compound relation, which could explain some transformation processes in the atmosphere.

## A.2 The First Plastic Produced but the Latest Studied in Microplastic Research: the Assessment of Leaching, Ecotoxicity and Bioadhesion of Bakelite Microplastics

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The second cooperation during my PhD resulted in a paper published in Environmental Pollution, where we investigated ecotoxicity of Bakelite microplastic to aquatic organisms. Bakelite is the first synthetic plastic made of phenol formaldehyde resin, which could in the aquatic environment leach to water and influence living organisms. The Bakelite toxic effect was studied on four aquatic organisms, testing the influence of its leachates and microplastic particles before and after leaching, whereas a crustacean (*Daphnia magna*) was inspected for changes in its mobility, a plant (*Lemna minor*) was investigated for the inhibition of specific growth rate and chlorophyll content, a bacterium (*Allivibrio fischeri*) was tested for inhibition of bioluminescence, and algae (*Pseudokirchneriella subcapitata*) was again investigated for the inhibition of specific growth rate. The Bakelite leachates were produced separately in the medium specific for every organism. My contribution to the paper was the determination of phenol leached in the medium with the LC-MS method for simple phenols that was developed in the frame of the PhD and described in this dissertation. The method was originally developed for ambient PM extracts, but for the purpose of this research it was adapted for the measurement of simple phenols in environmental-like aqueous samples, which proves wider applicability of the developed method for environmental samples. Phenol has been determined in all of the leachates, except in the medium of the plant. This study confirms that Bakelite is not an inert microplastic and that phenol and phenol-like compounds leach into the environment and influence aquatic organisms.

# References

[1] D. Fowler *et al.*, "A chronology of global air quality," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* vol. 378, no. 2183, p. 20190314, 2020, doi: doi:10.1098/rsta.2019.0314.

[2] T. M. Chen, S. Shofer, J. Gokhale, and W. G. Kuschner, "Outdoor air pollution: Overview and historical perspective," (in English), *Am. J. Med. Sci.,* Article vol. 333, no. 4, pp. 230-234, Apr 2007, doi: 10.1097/MAJ.0b013e31803b8c91.

[3] P. Brimblecombe, "The Big Smoke: A History of Air Pollution in London since Medieval Times (1st ed.)," *Routledge,* 1987, doi: https://doi.org/10.4324/9780203813898.

[4] T. Tzamkiozis, L. Ntziachristos, and Z. Samaras, "Diesel passenger car PM emissions: From Euro 1 to Euro 4 with particle filter," *Atmos. Environ.,* vol. 44, no. 7, pp. 909-916, 2010/03/01/ 2010, doi: https://doi.org/10.1016/j.atmosenv.2009.12.003.

[5] M. Crippa *et al.*, "Forty years of improvements in European air quality: regional policy-industry interactions with global impacts," *Atmos. Chem. Phys.,* vol. 16, no. 6, pp. 3825-3841, 2016, doi: 10.5194/acp-16-3825-2016.

[6] J. Turner and I. Colbeck, "Physical and Chemical Properties of Atmospheric Aerosols," in *Environmental Chemistry of Aerosols*, I. Colbeck Ed., 1st ed. ed., 2008, ch. Chapter 1, pp. 1-29.

[7] S. Fuzzi *et al.*, "Particulate matter, air quality and climate: lessons learned and future needs," *Atmos. Chem. Phys.,* vol. 15, no. 14, pp. 8217-8299, 2015, doi: 10.5194/acp-15-8217-2015.

[8] IPCC, "Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change," Cambridge, United Kingdom and New York, 2013.

[9] A. López-Caravaca *et al.*, "Combination of PM optical and chemical properties to estimate the contribution of non-BC absorbers to light absorption at a remote site," *Atmos. Res.,* vol. 268, p. 106000, 2022/04/15/ 2022, doi: https://doi.org/10.1016/j.atmosres.2021.106000.

[10] C. Mohr *et al.*, "Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time," (in English), *Environmental Science & Technology,* Article vol. 47, no. 12, pp. 6316-6324, Jun 2013, doi: 10.1021/es400683v.

[11] H. Al-Thani, M. Koc, and R. J. Isaifan, "A review on the direct effect of particulate atmospheric pollution on materials and its mitigation for sustainable cities and

societies," *Environ. Sci. Pollut. Res.,* vol. 25, no. 28, pp. 27839-27857, Oct 2018, doi: 10.1007/s11356-018-2952-8.

[12] P. Liu *et al.*, "Resolving the mechanisms of hygroscopic growth and cloud condensation nuclei activity for organic particulate matter," *Nature Communications,* vol. 9, no. 1, p. 4076, 2018/10/04 2018, doi: 10.1038/s41467-018-06622-2.

[13] N. P. Hyslop, "Impaired visibility: the air pollution people see," (in English), *Atmos. Environ.,* Review vol. 43, no. 1, pp. 182-195, Jan 2009, doi: 10.1016/j.atmosenv.2008.09.067.

[14] S. Q. Zheng, J. H. Wang, C. Sun, X. N. Zhang, and M. E. Kahn, "Air pollution lowers Chinese urbanites' expressed happiness on social media," (in English), *Nat. Hum. Behav.,* Article vol. 3, no. 3, pp. 237-243, Mar 2019, doi: 10.1038/s41562-018-0521-2.

[15] C. Eusébio *et al.*, "The impact of air quality on tourism: a systematic literature review," (in English), *J. Tour. Futur.,* Article 2020, doi: 10.1108/JTF-06-2019-0049.

[16] M. Shahid, C. Dumat, S. Khalid, E. Schreck, T. T. Xiong, and N. K. Niazi, "Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake," *J. Hazard. Mater.,* Review vol. 325, pp. 36-58, Mar 2017, doi: 10.1016/j.jhazmat.2016.11.063.

[17] D. A. Grantz, J. H. B. Garner, and D. W. Johnson, "Ecological effects of particulate matter," (in English), *Environ. Int.,* Article; Proceedings Paper vol. 29, no. 2-3, pp. 213-239, Jun 2003, doi: 10.1016/s0160-4120(02)00181-2.

[18] M. Adamek *et al.*, "Toxicity of nitrophenolic pollutant 4-nitroguaiacol to terrestrial plants and comparison with its non-nitro analogue guaiacol (2-methoxyphenol)," *(submitted, in review),* 2022.

[19] EEA, "Air quality in Europe - 2020 report," 1977-8449, 2020.

[20] M. Natangelo, S. Mangiapan, R. Bagnati, E. Benfenati, and R. Fanelli, "Increased concentrations of nitrophenols in leaves from a damaged forestal site," *Chemosphere,* vol. 38, no. 7, pp. 1495-1503, 1999/03/01/ 1999, doi: https://doi.org/10.1016/S0045-6535(98)00370-1.

[21] A. Milinković *et al.*, "Variabilities of biochemical properties of the sea surface microlayer: Insights to the atmospheric deposition impacts," *Sci. Total Environ.,* vol. 838, p. 156440, 2022/09/10/ 2022, doi: https://doi.org/10.1016/j.scitotenv.2022.156440.

[22] A. Paytan *et al.*, "Toxicity of atmospheric aerosols on marine phytoplankton," (in English), *Proc. Natl. Acad. Sci. U. S. A.,* Article vol. 106, no. 12, pp. 4601-4605, Mar 2009, doi: 10.1073/pnas.0811486106.

[23] S. Babić *et al.*, "Utilization of the zebrafish model to unravel the harmful effects of biomass burning during Amazonian wildfires," (in English), *Sci Rep,* Article vol. 11, no. 1, p. 12, Jan 2021, Art no. 2527, doi: 10.1038/s41598-021-81789-1.

[24] B. Wei, J. F. Sun, Q. Mei, Z. X. An, X. Y. Wang, and M. X. He, "Theoretical study on gas-phase reactions of nitrate radicals with methoxyphenols: Mechanism, kinetic and toxicity assessment," (in English), *Environ. Pollut.,* Article vol. 243, pp. 1772-1780, Dec 2018, doi: 10.1016/j.envpol.2018.08.104.

[25] Z. X. An *et al.*, "Theoretical study on the mechanisms, kinetics and ecotoxicity assessment of OH-initiated reactions of guaiacol in atmosphere and wastewater," (in English), *Sci. Total Environ.,* Article vol. 685, pp. 729-740, Oct 2019, doi: 10.1016/j.scitotenv.2019.06.229.

[26] M. Pflieger and A. Kroflič, "Acute toxicity of emerging atmospheric pollutants from wood lignin due to biomass burning," (in English), *J. Hazard. Mater.,* Article vol. 338, pp. 132-139, Sep 2017, doi: 10.1016/j.jhazmat.2017.05.023.

[27] E. Calparsoro, M. Maguregui, A. Giakoumaki, H. Morillas, and J. M. Madariaga, "Evaluation of black crust formation and soiling process on historical buildings from the Bilbao metropolitan area (north of Spain) using SEM-EDS and Raman microscopy," *Environ. Sci. Pollut. Res.,* vol. 24, no. 10, pp. 9468-9480, 2017/04/01 2017, doi: 10.1007/s11356-017-8518-3.

[28] M. F. La Russa *et al.*, "Geochemical study of black crusts as a diagnostic tool in cultural heritage," *Applied Physics A,* vol. 113, no. 4, pp. 1151-1162, 2013/12/01 2013, doi: 10.1007/s00339-013-7912-z.

[29] C. M. Belfiore *et al.*, "Application of spectrometric analysis to the identification of pollution sources causing cultural heritage damage," *Environ. Sci. Pollut. Res.,* vol. 20, no. 12, pp. 8848-8859, 2013/12/01 2013, doi: 10.1007/s11356-013-1810-y.

[30] C. Rodriguez-Navarro and E. Sebastian, "Role of particulate matter from vehicle exhaust on porous building stones (limestone) sulfation," *Sci. Total Environ.,* vol. 187, no. 2, pp. 79-91, 1996/08/30/ 1996, doi: https://doi.org/10.1016/0048-9697(96)05124-8.

[31] A. Bonazza, C. Sabbioni, and N. Ghedini, "Quantitative data on carbon fractions in interpretation of black crusts and soiling on European built heritage," *Atmos. Environ.,* vol. 39, no. 14, pp. 2607-2618, 2005/05/01/ 2005, doi: https://doi.org/10.1016/j.atmosenv.2005.01.040.

[32] M. H. Forouzanfar *et al.*, "Global, regional, and national comparative risk assessment of 79 behavioural, environmental and occupational, and metabolic risks or clusters of risks, 1990&#x2013;2015: a systematic analysis for the Global Burden of Disease Study 2015," *The Lancet,* vol. 388, no. 10053, pp. 1659-1724, 2016, doi: 10.1016/S0140-6736(16)31679-8.

[33] A. Valavanidis, K. Fiotakis, and T. Vlachogianni, "Airborne Particulate Matter and Human Health: Toxicological Assessment and Importance of Size and Composition of Particles for Oxidative Damage and Carcinogenic Mechanisms," *Journal of Environmental Science and Health, Part C,* vol. 26, no. 4, pp. 339-362, 2008/12/02 2008, doi: 10.1080/10590500802494538.

[34] H. Wu *et al.*, "Short-term effects of exposure to ambient PM1, PM2.5, and PM10 on ischemic and hemorrhagic stroke incidence in Shandong Province, China," *Environ. Res.,* vol. 212, p. 113350, 2022/09/01/ 2022, doi: https://doi.org/10.1016/j.envres.2022.113350.

[35] J. H. Choi, J. S. Kim, Y. C. Kim, Y. S. Kim, N. H. Chung, and M. H. Cho, "Comparative study of PM2.5 - and PM10 - induced oxidative stress in rat lung epithelial cells," *Journal of Veterinary Science,* vol. 5, no. 1, pp. 11-18, 02 2004, doi: 10.4142/jvs.2004.5.1.11.

[36] C. Reche *et al.*, "A multidisciplinary approach to characterise exposure risk and toxicological effects of PM10 and PM2.5 samples in urban environments," *Ecotox. Environ. Safe.,* vol. 78, pp. 327-335, 2012/04/01/ 2012, doi: https://doi.org/10.1016/j.ecoenv.2011.11.043.

[37] G. Oberdörster *et al.*, "Translocation of Inhaled Ultrafine Particles to the Brain," *Inhal. Toxicol.,* vol. 16, no. 6-7, pp. 437-445, 2004/01/01 2004, doi: 10.1080/08958370490439597.

[38] W. Li *et al.*, "A review of respirable fine particulate matter (PM2.5)-induced brain damage," (in English), *Frontiers in Molecular Neuroscience,* Review vol. 15, 2022-September-07 2022, doi: 10.3389/fnmol.2022.967174.

[39] R. You, Y.-S. Ho, and R. C.-C. Chang, "The pathogenic effects of particulate matter on neurodegeneration: a review," *Journal of Biomedical Science,* vol. 29, no. 1, p. 15, 2022/02/22 2022, doi: 10.1186/s12929-022-00799-x.

[40] K. Straif, A. Cohen, and J. Samet, "Air pollution and Cancer," *IARC Scientific Publications,* vol. 161, 2013.

[41] D. Loomis, W. Huang, and G. S. Chen, "The International Agency for Research on Cancer (IARC) evaluation of the carcinogenicity of outdoor air pollution: focus on China," (in English), *Chin. J. Cancer,* Review vol. 33, no. 4, pp. 189-196, Apr 2014, doi: 10.5732/cjc.014.10028.

[42] EEA, "Air quality in Europe - 2019 report," 1977-8449, 2019.

[43] X. Wang *et al.*, "Comprehensive pulmonary metabolome responses to intratracheal instillation of airborne fine particulate matter in rats," *Sci. Total Environ.,* vol. 592, pp. 41-50, 2017/08/15/ 2017, doi: https://doi.org/10.1016/j.scitotenv.2017.03.064.

[44] N. Schweigert, A. J. B. Zehnder, and R. I. L. Eggen, "Chemical properties of catechols and their molecular modes of toxic action in cells, from microorganisms to mammals," (in English), *Environ. Microbiol.,* Review vol. 3, no. 2, pp. 81-91, Feb 2001, doi: 10.1046/j.1462-2920.2001.00176.x.

[45] E. Ahmed, K. Nagaoka, M. Fayez, M. M. Abdel-Daim, H. Samir, and G. Watanabe, "Suppressive effects of long-term exposure to P-nitrophenol on gonadal development, hormonal profile with disruption of tissue integrity, and activation of caspase-3 in male Japanese quail (Coturnix japonica)," (in English), *Environ. Sci. Pollut. Res.,* Article vol. 22, no. 14, pp. 10930-10942, Jul 2015, doi: 10.1007/s11356-015-4245-9.

[46] F. Khan *et al.*, "Cytotoxicity and oxidative stress induced by atmospheric mono-nitrophenols in human lung cells," *Environ. Pollut.,* vol. 301, p. 119010, 2022/05/15/ 2022, doi: https://doi.org/10.1016/j.envpol.2022.119010.

[47] X. Z. Li, C. M. Li, A. K. Suzuki, S. Taneda, G. Watanabe, and K. Taya, "4-Nitrophenol isolated from diesel exhaust particles disrupts regulation of reproductive hormones in immature male rats," (in English), *Endocrine,* Article vol. 36, no. 1, pp. 98-102, Aug 2009, doi: 10.1007/s12020-009-9192-0.

[48] M. Majewska, F. Khan, I. S. Pieta, A. Wróblewska, R. Szmigielski, and P. Pieta, "Toxicity of selected airborne nitrophenols on eukaryotic cell membrane models,"

*Chemosphere,* vol. 266, p. 128996, 2021/03/01/ 2021, doi: https://doi.org/10.1016/j.chemosphere.2020.128996.

[49] S. Taneda *et al.*, "Estrogenic and anti-androgenic activity of nitrophenols in diesel exhaust particles (DEP)," (in English), *Biol. Pharm. Bull.,* Article vol. 27, no. 6, pp. 835-837, Jun 2004, doi: 10.1248/bpb.27.835.

[50] J. J. Ran *et al.*, "Effects of particulate matter exposure on the transmissibility and case fatality rate of COVID-19: A Nationwide Ecological Study in China," (in English), *J. Travel Med.,* Letter vol. 27, no. 6, p. 4, Aug 2020, Art no. taaa133, doi: 10.1093/jtm/taaa133.

[51] X. Wu, R. C. Nethery, M. B. Sabath, D. Braun, and F. Dominici, "Exposure to air pollution and COVID-19 mortality in the United States: A nationwide cross-sectional study," *medRxiv,* p. 2020.04.05.20054502, 2020, doi: 10.1101/2020.04.05.20054502.

[52] S. W. Wu *et al.*, "Chemical constituents of fine particulate air pollution and pulmonary function in healthy adults: The Healthy Volunteer Natural Relocation study," (in English), *J. Hazard. Mater.,* Article vol. 260, pp. 183-191, Sep 2013, doi: 10.1016/j.jhazmat.2013.05.018.

[53] W. John, "Size Distribution Characteristics of Aerosols," in *Aerosol Measurement*, P. Kulkarni, P. A. Baron, and K. Willeke Eds., 3rd ed. ed.: John Wiley & Sons, Inc., 2011, ch. 4, pp. 41-54.

[54] W. C. Hinds, "Physical and chemical processes in aerosol systems," in *Aerosol Measurement*, P. Kulkarni, P. A. Baron, and K. Willeke Eds.: John Wiley & Sons, Inc., 2011, ch. 3, pp. 31-40.

[55] M. Hallquist *et al.*, "The formation, properties and impact of secondary organic aerosol: current and emerging issues," *Atmos. Chem. Phys.,* vol. 9, no. 14, pp. 5155-5236, 2009, doi: 10.5194/acp-9-5155-2009.

[56] E. A. Bruns *et al.*, "Identification of significant precursor gases of secondary organic aerosols from residential wood combustion," *Sci Rep,* vol. 6, no. 1, p. 27881, 2016/06/17 2016, doi: 10.1038/srep27881.

[57] C. A. Belis *et al.*, "European guide on air pollution source apportionment with receptor models - Revised version 2019," in "EUR 29816 EN," Publications Office of the European Union, Luxembourg, 2019.

[58] C. A. Belis, F. Karagulian, B. R. Larsen, and P. K. Hopke, "Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe," *Atmos. Environ.,* Review vol. 69, pp. 94-108, Apr 2013, doi: 10.1016/j.atmosenv.2012.11.009.

[59] C. A. Belis *et al.*, "Source apportionment of fine PM by combining high time resolution organic and inorganic chemical composition datasets," (in English), *Atmos. Environ-X,* Article vol. 3, p. 15, Jul 2019, Art no. 100046, doi: 10.1016/j.aeaoa.2019.100046.

[60] P. K. Hopke, Q. L. Dai, L. X. Li, and Y. C. Feng, "Global review of recent source apportionments for airborne particulate matter," *Sci. Total Environ.,* Review vol. 740, p. 10, Oct 2020, Art no. 140091, doi: 10.1016/j.scitotenv.2020.140091.

[61] D. Cesari, F. Amato, M. Pandolfi, A. Alastuey, X. Querol, and D. Contini, "An inter-comparison of PM10 source apportionment using PCA and PMF receptor models in three European sites," (in English), *Environ. Sci. Pollut. Res.,* Article vol. 23, no. 15, pp. 15133-15148, Aug 2016, doi: 10.1007/s11356-016-6599-z.

[62] G. Norris, R. Duvall, S. Brown, and S. Bai, "EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide," U.S. Environmental Protection Agency, Washington, DC, 2014, vol. EPA/600/R-14/108.

[63] M. Sillanpää *et al.*, "Chemical composition and mass closure of particulate matter at six urban sites in Europe," *Atmos. Environ.,* vol. 40, pp. 212-223, 2006/01/01/ 2006, doi: https://doi.org/10.1016/j.atmosenv.2006.01.063.

[64] T. Koleša and A. Planinšek, "Opredelitev virov delcev PM10 v Ljubljani," Agencija RS za okolje, 2013.

[65] Q. Wang *et al.*, "Source Apportionment of PM2.5 Using Hourly Measurements of Elemental Tracers and Major Constituents in an Urban Environment: Investigation of Time-Resolution Influence," *Journal of Geophysical Research: Atmospheres,* vol. 123, no. 10, pp. 5284-5300, 2018, doi: https://doi.org/10.1029/2017JD027877.

[66] Y. Li, M. Chang, S. Ding, S. Wang, D. Ni, and H. Hu, "Monitoring and source apportionment of trace elements in PM2.5: Implications for local air quality management," (in English), *J. Environ. Manage.,* Article vol. 196, pp. 16-25, 2017, doi: 10.1016/j.jenvman.2017.02.059.

[67] S. K. Akagi *et al.*, "Emission factors for open and domestic biomass burning for use in atmospheric models," *Atmos. Chem. Phys.,* vol. 11, no. 9, pp. 4039-4072, 2011, doi: 10.5194/acp-11-4039-2011.

[68] C. E. Stockwell, P. R. Veres, J. Williams, and R. J. Yokelson, "Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry," *Atmos. Chem. Phys.,* vol. 15, no. 2, pp. 845-865, 2015, doi: 10.5194/acp-15-845-2015.

[69] M. Campen, S. Robertson, A. Lund, J. Lucero, and J. McDonald, "Engine exhaust particulate and gas phase contributions to vascular toxicity," (in English), *Inhal. Toxicol.,* Article vol. 26, no. 6, pp. 353-360, May 2014, doi: 10.3109/08958378.2014.897776.

[70] E. A. Pillar and M. I. Guzman, "Oxidation of Substituted Catechols at the Air-Water Interface: Production of Carboxylic Acids, Quinones, and Polyphenols," (in English), *Environmental Science & Technology,* Article vol. 51, no. 9, pp. 4951-4959, May 2017, doi: 10.1021/acs.est.7b00232.

[71] Z. Finewax, J. A. de Gouw, and P. J. Ziemann, "Identification and Quantification of 4-Nitrocatechol Formed from OH and NO3 Radical-Initiated Reactions of Catechol in Air in the Presence of NOx: Implications for Secondary Organic Aerosol Formation from Biomass Burning," (in English), *Environmental Science & Technology,* Article vol. 52, no. 4, pp. 1981-1989, Feb 2018, doi: 10.1021/acs.est.7b05864.

[72] A. Kroflič *et al.*, "Guaiacol Nitration in a Simulated Atmospheric Aerosol with an Emphasis on Atmospheric Nitrophenol Formation Mechanisms," (in English), *Acs*

*Earth and Space Chemistry,* Article vol. 5, no. 5, pp. 1083-1093, May 2021, doi: 10.1021/acsearthspacechem.1c00014.

[73] K. Vidović, A. Kroflič, P. Jovanovič, M. Šala, and I. Grgić, "Electrochemistry as a Tool for Studies of Complex Reaction Mechanisms: The Case of the Atmospheric Aqueous-Phase Aging of Catechols," *Environmental Science & Technology,* vol. 53, no. 19, pp. 11195-11203, 2019/10/01 2019, doi: 10.1021/acs.est.9b02456.

[74] K. Vidović, D. Lašič Jurković, M. Šala, A. Kroflič, and I. Grgić, "Nighttime Aqueous-Phase Formation of Nitrocatechols in the Atmospheric Condensed Phase," *Environmental Science & Technology,* vol. 52, no. 17, pp. 9722-9730, 2018/09/04 2018, doi: 10.1021/acs.est.8b01161.

[75] A. Kroflič, M. Grilc, and I. Grgić, "Unraveling Pathways of Guaiacol Nitration in Atmospheric Waters: Nitrite, A Source of Reactive Nitronium Ion in the Atmosphere," *Environmental Science & Technology,* vol. 49, no. 15, pp. 9150-9158, 2015/08/04 2015, doi: 10.1021/acs.est.5b01811.

[76] Y. Iinuma, O. Boge, R. Grafe, and H. Herrmann, "Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols," (in English), *Environmental Science & Technology,* Article vol. 44, no. 22, pp. 8453-8459, Nov 2010, doi: 10.1021/es102938a.

[77] J. Ofner, H. U. Kruger, H. Grothe, P. Schmitt-Kopplin, K. Whitmore, and C. Zetzsch, "Physico-chemical characterization of SOA derived from catechol and guaiacol - a model substance for the aromatic fraction of atmospheric HULIS," (in English), *Atmos. Chem. Phys.,* Article vol. 11, no. 1, pp. 1-15, 2011, doi: 10.5194/acp-11-1-2011.

[78] A. Albinet, G. M. Lanzafame, D. Srivastava, N. Bonnaire, F. Nalin, and S. A. Wise, "Analysis and determination of secondary organic aerosol (SOA) tracers (markers) in particulate matter standard reference material (SRM 1649b, urban dust)," (in English), *Anal. Bioanal. Chem.,* Article vol. 411, no. 23, pp. 5975-5983, Sep 2019, doi: 10.1007/s00216-019-02015-6.

[79] B. R. T. Simonelt, "A review of current applications of mass spectrometry for biomarker/molecular tracer elucidations," (in English), *Mass Spectrom. Rev.,* Review vol. 24, no. 5, pp. 719-765, Sep-Oct 2005, doi: 10.1002/mas.20036.

[80] Z. Kitanovski, I. Grgic, F. Yasmeen, M. Claeys, and A. Cusak, "Development of a liquid chromatographic method based on ultraviolet-visible and electrospray ionization mass spectrometric detection for the identification of nitrocatechols and related tracers in biomass burning atmospheric organic aerosol," (in English), *Rapid Commun. Mass Spectrom.,* Article vol. 26, no. 7, pp. 793-804, Apr 2012, doi: 10.1002/rcm.6170.

[81] S. Frka, I. Grgic, J. Tursic, M. I. Gini, and K. Eleftheriadis, "Seasonal variability of carbon in humic-like matter of ambient size segregated water soluble organic aerosols from urban background environment," (in English), *Atmos. Environ.,* Article vol. 173, pp. 239-247, Jan 2018, doi: 10.1016/j.atmosenv.2017.11.013.

[82] M. Li *et al.*, "Nitrated phenols and the phenolic precursors in the atmosphere in urban Jinan, China," (in English), *Sci. Total Environ.,* Article vol. 714, p. 10, Apr 2020, Art no. 136760, doi: 10.1016/j.scitotenv.2020.136760.

[83] S. Frka, M. Šala, H. Brodnik, B. Štefane, A. Kroflič, and I. Grgić, "Seasonal variability of nitroaromatic compounds in ambient aerosols: Mass size distribution, possible sources and contribution to water-soluble brown carbon light absorption," *Chemosphere,* vol. 299, p. 134381, 2022, doi: https://doi.org/10.1016/j.chemosphere.2022.134381.

[84] A. Colette and L. Rouil, "Air quality trends in Europe: 2000-2017," in "Eionet Report - ETC/ATNI 2019/16," EEA, 2020.

[85] F. J. Kelly, G. W. Fuller, H. A. Walton, and J. C. Fussell, "Monitoring air pollution: Use of early warning systems for public health," *Respirology,* vol. 17, no. 1, pp. 7-19, 2012, doi: https://doi.org/10.1111/j.1440-1843.2011.02065.x.

[86] CEN, "EN 14902:2005, Ambient air quality. Standard method for the measurement of Pb, Cd, As, and Ni in the PM 10 fraction of suspended particulate matter," 2005.

[87] World Health Organization, *WHO global air quality guidelines: particulate matter (PM2.5 and PM10), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide.* Geneva: World Health Organization (in en), 2021.

[88] L. Drinovec *et al.*, "The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation," (in English), *Atmos. Meas. Tech.,* Article vol. 8, no. 5, pp. 1965-1979, 2015, doi: 10.5194/amt-8-1965-2015.

[89] M. Rigler *et al.*, "The new instrument using a TC-BC (total carbon-black carbon) method for the online measurement of carbonaceous aerosols," (in English), *Atmos. Meas. Tech.,* Article vol. 13, no. 8, pp. 4333-4351, Aug 2020, doi: 10.5194/amt-13-4333-2020.

[90] F. D. Lopez-Hilfiker *et al.*, "A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO)," *Atmos. Meas. Tech.,* vol. 7, no. 4, pp. 983-1001, 2014, doi: 10.5194/amt-7-983-2014.

[91] Y. J. Li *et al.*, "Real-time chemical characterization of atmospheric particulate matter in China: A review," (in English), *Atmos. Environ.,* Review vol. 158, pp. 270-304, Jun 2017, doi: 10.1016/j.atmosenv.2017.02.027.

[92] P. Avino, G. Capannesi, F. Lopez, and A. Rosada, "Determination of Interesting Toxicological Elements in PM2.5 by Neutron and Photon Activation Analysis," (in English), *Sci. World J.,* Article p. 8, 2013, Art no. 458793, doi: 10.1155/2013/458793.

[93] M. S. Robinson, I. Grgic, V. S. Selih, M. Sala, M. Bitsui, and J. T. van Elteren, "Laser ablation ICP-MS of size-segregated atmospheric particles collected with a MOUDI cascade impactor: a proof of concept," (in English), *Atmos. Meas. Tech.,* Article vol. 10, no. 5, pp. 1823-1830, May 2017, doi: 10.5194/amt-10-1823-2017.

[94] S. Yatkin *et al.*, "Evaluation of EDXRF for the Determination of Elements in PM10 Filters, EUR 24983 EN," *Publication Office of the European Union, Luxemburg,* 2011, doi: 10.2788/87284.

[95] D. Günther and B. Hattendorf, "Solid sample analysis using laser ablation inductively coupled plasma mass spectrometry," *TrAC Trends in Analytical*

*Chemistry,* vol. 24, no. 3, pp. 255-265, 2005/03/01/ 2005, doi: https://doi.org/10.1016/j.trac.2004.11.017.

[96] C. Ludke, E. Hoffmann, and J. Skole, "Comparative-studies on metal determination in airborne-particulates by LA-ICP-MS and furnace atomization nonthermal excitation spectrometry," (in English), *Fresenius J. Anal. Chem.,* Article; Proceedings Paper vol. 350, no. 4-5, pp. 272-276, Oct 1994, doi: 10.1007/bf00322481.

[97] C. J. Chin, C. F. Wang, and S. L. Jeng, "Multi-element analysis of airborne particulate matter collected on PTFE-membrane filters by laser ablation inductively coupled plasma mass spectrometry," (in English), *J. Anal. At. Spectrom.,* Article vol. 14, no. 4, pp. 663-668, Apr 1999, doi: 10.1039/a807275b.

[98] C. F. Wang, C. J. Chin, S. K. Luo, and L. C. Men, "Determination of chromium in airborne particulate matter by high resolution and laser ablation inductively coupled plasma mass spectrometry," (in English), *Anal. Chim. Acta,* Article vol. 389, no. 1-3, pp. 257-266, May 1999, doi: 10.1016/s0003-2670(99)00162-2.

[99] S. Tanaka *et al.*, "Rapid and simultaneous multi-element analysis of atmospheric particulate matter using inductively coupled plasma mass spectrometry with laser ablation sample introduction," (in English), *J. Anal. At. Spectrom.,* Article vol. 13, no. 2, pp. 135-140, Feb 1998, doi: 10.1039/a705597h.

[100] L. Qiao, R. Zhang, J. Qiao, X. He, and Z. Wu, "Preparation of ashless cellulose paper standards for rapid determination of multi-element concentrations in airborne fine particulate matter using laser ablation inductively coupled plasma mass spectrometry," (in English), *RSC Adv.,* Article vol. 11, no. 12, pp. 6644-6653, 2021, doi: 10.1039/d0ra09200b.

[101] S. Rovelli, W. Nischkauer, D. M. Cavallo, and A. Limbeck, "Multi-element analysis of size-segregated fine and ultrafine particulate via Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry," (in English), *Anal. Chim. Acta,* Article vol. 1043, pp. 11-19, Dec 2018, doi: 10.1016/j.aca.2018.10.026.

[102] X. X. Tang *et al.*, "Analysis of atmospheric pollutant metals by laser ablation inductively coupled plasma mass spectrometry with a radial line-scan dried-droplet approach," (in English), *Spectroc. Acta Pt. B-Atom. Spectr.,* Article vol. 138, pp. 18-22, Dec 2017, doi: 10.1016/j.sab.2017.09.015.

[103] M. Guillong, I. Horn, and D. Gunther, "A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd : YAG laser for laser ablation ICP-MS," (in English), *J. Anal. At. Spectrom.,* Article vol. 18, no. 10, pp. 1224-1230, 2003, doi: 10.1039/b305434a.

[104] M. Guillong and D. Gunther, "Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry," (in English), *J. Anal. At. Spectrom.,* Article vol. 17, no. 8, pp. 831-837, 2002, doi: 10.1039/b202988j.

[105] R. J. C. Brown, K. E. Jarvis, B. A. Disch, S. L. Goddard, and A. S. Brown, "Spatial inhomogeneity of metals in particulate matter on ambient air filters determined by LA-ICP-MS and comparison with acid digestion ICP-MS," (in English), *J. Environ. Monit.,* Article vol. 11, no. 11, pp. 2022-2029, 2009, doi: 10.1039/b911441f.

[106] R. J. C. Brown, K. E. Jarvis, B. A. Disch, S. L. Goddard, E. Adriaenssens, and N. Claeys, "Comparison of ED-XRF and LA-ICP-MS with the European reference method of acid digestion-ICP-MS for the measurement of metals in ambient particulate matter," (in English), *Accredit. Qual. Assur.,* Article vol. 15, no. 9, pp. 493-502, Sep 2010, doi: 10.1007/s00769-010-0668-7.

[107] R. J. C. Brown, K. E. Jarvis, B. A. Disch, and S. L. Goddard, "An investigation of calibration materials for the measurement of metals in ambient particulate matter on filters by LA-ICP-MS," (in English), *Int. J. Environ. Anal. Chem.,* Article vol. 93, no. 3, pp. 335-348, Mar 2013, doi: 10.1080/03067319.2011.592950.

[108] C. F. Wang, S. L. Jeng, C. C. Lin, and P. C. Chiang, "Preparation of airborne particulate standards on PTFE-membrane filter for laser ablation inductively coupled plasma mass spectrometry," (in English), *Anal. Chim. Acta,* Article vol. 368, no. 1-2, pp. 11-19, Jul 1998, doi: 10.1016/s0003-2670(98)00028-2.

[109] Y. K. Hsieh, L. K. Chen, H. F. Hsieh, C. H. Huang, and C. F. Wang, "Elemental analysis of airborne particulate matter using an electrical low-pressure impactor and laser ablation/inductively coupled plasma mass spectrometry," (in English), *J. Anal. At. Spectrom.,* Article vol. 26, no. 7, pp. 1502-1508, 2011, doi: 10.1039/c0ja00207k.

[110] T. M. Do, C. F. Wang, Y. K. Hsieh, and H. F. Hsieh, "Metals Present in Ambient Air before and after a Firework Festival in Yanshui, Tainan, Taiwan," (in English), *Aerosol Air Qual. Res.,* Article vol. 12, no. 5, pp. 981-993, Oct 2012, doi: 10.4209/aaqr.2012.03.0069.

[111] S. Rovelli *et al.*, "Toxic trace metals in size-segregated fine particulate matter: Mass concentration, respiratory deposition, and risk assessment," (in English), *Environ. Pollut.,* Article vol. 266, p. 10, Nov 2020, Art no. 115242, doi: 10.1016/j.envpol.2020.115242.

[112] T. Okuda *et al.*, "Daily concentrations of trace metals in aerosols in Beijing, China, determined by using inductively coupled plasma mass spectrometry equipped with laser ablation analysis, and source identification of aerosols," (in English), *Sci. Total Environ.,* Article vol. 330, no. 1-3, pp. 145-158, Sep 2004, doi: 10.1016/j.scitotenv.2004.04.010.

[113] W. Nischkauer, A. Izmer, M. A. Neouze, F. Vanhaecke, and A. Limbeck, "Combining Dispersed Particle Extraction with Dried-Droplet Laser Ablation ICP-MS for Determining Platinum in Airborne Particulate Matter," (in English), *APPL.SPECTROSC.,* Article vol. 71, no. 7, pp. 1613-1620, Jul 2017, doi: 10.1177/0003702817693240.

[114] S. Gligorovski, J. T. Elteren, and I. Grgic, "A multi-element mapping approach for size-segregated atmospheric particles using laser ablation ICP-MS combined with image analysis," (in English), *Sci. Total Environ.,* Article vol. 407, no. 1, pp. 594-602, Dec 2008, doi: 10.1016/j.scitotenv.2008.09.017.

[115] A. Villasenor, C. Greatti, M. Boccongelli, and J. L. Todoli, "A dried droplet calibration approach for the analysis of solid samples through laser ablation - inductively coupled plasma mass spectrometry," (in English), *J. Anal. At. Spectrom.,* Article vol. 32, no. 3, pp. 587-596, Mar 2017, doi: 10.1039/c6ja00343e.

[116] M. Burger *et al.*, "High-speed, high-resolution, multielemental LA-ICP-TOFMS imaging: part II. critical evaluation of quantitative three-dimensional imaging of major, minor, and trace elements in geological samples," (in eng), *Anal. Chem.,* vol. 87, no. 16, pp. 8259-8267, 2015/08// 2015, doi: 10.1021/acs.analchem.5b01977.

[117] J. C. Chow *et al.*, "The IMPROVE-A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database," (in English), *J. Air Waste Manage. Assoc.,* Article vol. 57, no. 9, pp. 1014-1023, Sep 2007, doi: 10.3155/1047-3289.57.9.1014.

[118] F. Cavalli, M. Viana, K. E. Yttri, J. Genberg, and J. P. Putaud, "Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol," (in English), *Atmos. Meas. Tech.,* Article vol. 3, no. 1, pp. 79-89, 2010, doi: 10.5194/amt-3-79-2010.

[119] J. Yus-Diez *et al.*, "Determination of the multiple-scattering correction factor and its cross-sensitivity to scattering and wavelength dependence for different AE33 Aethalometer filter tapes: a multi-instrumental approach," (in English), *Atmos. Meas. Tech.,* Article vol. 14, no. 10, pp. 6335-6355, Oct 2021, doi: 10.5194/amt-14-6335-2021.

[120] L. Ferrero *et al.*, "Consistent determination of the heating rate of light-absorbing aerosol using wavelength- and time-dependent Aethalometer multiple-scattering correction," (in English), *Sci. Total Environ.,* Article vol. 791, p. 19, Oct 2021, Art no. 148277, doi: 10.1016/j.scitotenv.2021.148277.

[121] X. Wu, T. V. Vu, Z. B. Shi, R. M. Harrison, D. Liu, and K. Cen, "Characterization and source apportionment of carbonaceous PM2.5 particles in China - A review," (in English), *Atmos. Environ.,* Review vol. 189, pp. 187-212, Sep 2018, doi: 10.1016/j.atmosenv.2018.06.025.

[122] J. Parshintsev and T. Hyotylainen, "Methods for characterization of organic compounds in atmospheric aerosol particles," (in English), *Anal. Bioanal. Chem.,* Review vol. 407, no. 20, pp. 5877-5897, Aug 2015, doi: 10.1007/s00216-014-8394-3.

[123] M. V. Johnston and D. E. Kerecman, "Molecular Characterization of Atmospheric Organic Aerosol by Mass Spectrometry," in *Annual Review of Analytical Chemistry, Vol 12*, vol. 12, P. W. Bohn and J. E. Pemberton Eds., (Annual Review of Analytical Chemistry. Palo Alto: Annual Reviews, 2019, pp. 247-274.

[124] I. Drventić, M. Šala, K. Vidović, and A. Kroflič, "Direct quantification of PAHs and nitro-PAHs in atmospheric PM by thermal desorption gas chromatography with electron ionization mass spectroscopic detection," *Talanta,* vol. 251, p. 123761, 2023/01/01/ 2023, doi: https://doi.org/10.1016/j.talanta.2022.123761.

[125] Z. Kitanovski, I. Grgić, R. Vermeylen, M. Claeys, and W. Maenhaut, "Liquid chromatography tandem mass spectrometry method for characterization of monoaromatic nitro-compounds in atmospheric particulate matter," (in English), *J. Chromatogr. A,* Article vol. 1268, pp. 35-43, Dec 2012, doi: 10.1016/j.chroma.2012.10.021.

[126] Z. Kitanovski, P. Shahpoury, C. Samara, A. Voliotis, and G. Lammel, "Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe -

implications for the origin," (in English), *Atmos. Chem. Phys.,* Article vol. 20, no. 4, pp. 2471-2487, Mar 2020, doi: 10.5194/acp-20-2471-2020.

[127] S. Frka, M. Šala, A. Kroflič, M. Huš, A. Čusak, and I. Grgić, "Quantum Chemical Calculations Resolved Identification of Methylnitrocatechols in Atmospheric Aerosols," (in English), *Environmental Science & Technology,* Article vol. 50, no. 11, pp. 5526-5535, Jun 2016, doi: 10.1021/acs.est.6b00823.

[128] A. Gentili, S. Marchese, and D. Perret, "MS techniques for analyzing phenols, their metabolites and transformation products of environmental interest," *TrAC Trends in Analytical Chemistry,* vol. 27, no. 10, pp. 888-903, 2008/11/01/ 2008, doi: https://doi.org/10.1016/j.trac.2008.07.008.

[129] D. Hoffmann, Y. Iinuma, and H. Herrmann, "Development of a method for fast analysis of phenolic molecular markers in biomass burning particles using high performance liquid chromatography/atmo spheric pressure chemical ionisation mass spectrometry," (in English), *J. Chromatogr. A,* Article vol. 1143, no. 1-2, pp. 168-175, Mar 2007, doi: 10.1016/j.chroma.2007.01.035.

[130] S. Samy and M. D. Hays, "Quantitative LC–MS for water-soluble heterocyclic amines in fine aerosols (PM2.5) at Duke Forest, USA," *Atmos. Environ.,* vol. 72, pp. 77-80, 2013/06/01/ 2013, doi: https://doi.org/10.1016/j.atmosenv.2013.02.032.

[131] Z. Kitanovski *et al.*, "Nitrated monoaromatic hydrocarbons (nitrophenols, nitrocatechols, nitrosalicylic acids) in ambient air: levels, mass size distributions and inhalation bioaccessibility," (in English), *Environ. Sci. Pollut. Res.,* Article vol. 28, no. 42, pp. 59131-59140, Nov 2021, doi: 10.1007/s11356-020-09540-3.

[132] F. Romero and M. Oehme, "Organosulfates – A New Component of Humic-Like Substances in Atmospheric Aerosols?," *Journal of Atmospheric Chemistry,* vol. 52, no. 3, pp. 283-294, 2005/11/01 2005, doi: 10.1007/s10874-005-0594-y.

[133] C. Leck, Q. Gao, F. Mashayekhy Rad, and U. Nilsson, "Size-resolved atmospheric particulate polysaccharides in the high summer Arctic," *Atmos. Chem. Phys.,* vol. 13, no. 24, pp. 12573-12588, 2013, doi: 10.5194/acp-13-12573-2013.

[134] B. R. Blackwell, Q. Cai, P. N. Smith, and G. P. Cobb, "Liquid chromatography-tandem mass spectrometry analysis of 17 alpha-trenbolone, 17 beta-trenbolone and trendione in airborne particulate matter," (in English), *Talanta,* Article vol. 85, no. 3, pp. 1317-1323, Sep 2011, doi: 10.1016/j.talanta.2011.06.011.

[135] C. Coscolla, E. Hart, A. Pastor, and V. Yusa, "LC-MS characterization of contemporary pesticides in PM10 of Valencia Region, Spain," (in English), *Atmos. Environ.,* Article vol. 77, pp. 394-403, Oct 2013, doi: 10.1016/j.atmosenv.2013.05.022.

[136] N. Mastroianni *et al.*, "Comprehensive monitoring of the occurrence of 22 drugs of abuse and transformation products in airborne particulate matter in the city of Barcelona," (in English), *Sci. Total Environ.,* Article vol. 532, pp. 344-352, Nov 2015, doi: 10.1016/j.scitotenv.2015.06.027.

[137] D. P. Patnana, B. P. Chandra, P. Chaudhary, B. Sinha, and V. Sinha, "Optimized LC-MS/MS method for simultaneous determination of endocrine disruptors and PAHs bound to PM2.5: Sources and health risk in Indo-Gangetic Plain," *Atmos.*

*Environ.,* vol. 290, p. 119363, 2022/12/01/ 2022, doi: https://doi.org/10.1016/j.atmosenv.2022.119363.

[138] J. Lintelmann, K. Fischer, and G. Matuschek, "Determination of oxygenated polycyclic aromatic hydrocarbons in particulate matter using high-performance liquid chromatography-tandem mass spectrometry," (in English), *J. Chromatogr. A,* Article vol. 1133, no. 1-2, pp. 241-247, Nov 2006, doi: 10.1016/j.chroma.2006.08.038.

[139] B.-L. Qi, P. Liu, Q.-Y. Wang, W.-J. Cai, B.-F. Yuan, and Y.-Q. Feng, "Derivatization for liquid chromatography-mass spectrometry," *TrAC Trends in Analytical Chemistry,* vol. 59, pp. 121-132, 2014/07/01/ 2014, doi: https://doi.org/10.1016/j.trac.2014.03.013.

[140] K. Guo, F. Bamforth, and L. A. Li, "Qualitative Metabolome Analysis of Human Cerebrospinal Fluid by C-13-/C-12-Isotope Dansylation Labeling Combined with Liquid Chromatography Fourier Transform Ion Cyclotron Resonance Mass Spectrometry," (in English), *J. Am. Soc. Mass Spectrom.,* Article vol. 22, no. 2, pp. 339-347, Feb 2011, doi: 10.1007/s13361-010-0033-4.

[141] K. Guo and L. Li, "Differential C-12/C-13-Isotope Dansylation Labeling and Fast Liquid Chromatography/Mass Spectrometry for Absolute and Relative Quantification of the Metabolome," (in English), *Anal. Chem.,* Article vol. 81, no. 10, pp. 3919-3932, May 2009, doi: 10.1021/ac900166a.

[142] W. X. Xu *et al.*, "Determination of phenolic compounds in estuary water and sediment by solid-phase isotope dansylation coupled with liquid chromatography-high resolution mass spectrometry," (in English), *Anal. Methods,* Article vol. 13, no. 11, pp. 1404-1411, Mar 2021, doi: 10.1039/d1ay00079a.

[143] Y. T. Chen *et al.*, "Targeting amine- and phenol-containing metabolites in urine by dansylation isotope labeling and liquid chromatography mass spectrometry for evaluation of bladder cancer biomarkers," (in English), *J. Food Drug Anal.,* Article vol. 27, no. 2, pp. 460-474, Apr 2019, doi: 10.1016/j.jfda.2018.11.008.

[144] H. Fan, B. Papouskova, K. Lemr, J. G. Wigginton, and K. A. Schug, "Bulk derivatization and direct injection of human cerebrospinal fluid for trace-level quantification of endogenous estrogens using trap-and-elute liquid chromatography with tandem mass spectrometry," (in English), *J. Sep. Sci.,* Article vol. 37, no. 15, pp. 2010-2017, Aug 2014, doi: 10.1002/jssc.201400165.

[145] Z. H. Wang *et al.*, "Simultaneous identification and quantification of bisphenol A and 12 bisphenol analogues in environmental samples using precolumn derivatization and ultra high performance liquid chromatography with tandem mass spectrometry," (in English), *J. Sep. Sci.,* Article vol. 41, no. 10, pp. 2269-2278, May 2018, doi: 10.1002/jssc.201701087.

[146] S. H. Yang, A. A. Morgan, H. P. Nguyen, H. Moore, B. J. Figard, and K. A. Schug, "Quantitative determination of bisphenol a from human saliva using bulk derivatization and trap-and-elute liquid chromatography coupled to electrospray ionization mass spectrometry," (in English), *Environ. Toxicol. Chem.,* Article vol. 30, no. 6, pp. 1243-1251, Jun 2011, doi: 10.1002/etc.498.

[147] S. Zhao and L. Li, "Chemical derivatization in LC-MS-based metabolomics study," *TrAC Trends in Analytical Chemistry,* vol. 131, p. 115988, 2020/10/01/ 2020, doi: https://doi.org/10.1016/j.trac.2020.115988.

# Bibliography

## Publications Related to the Thesis

## Journal Articles

M. Ogrizek, R. Jaćimović, M. Šala, and A. Kroflič, "No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters," Talanta, vol. 226, p. 122110, 2021/05/01/ 2021, doi: https://doi.org/10.1016/j.talanta.2021.122110.

Jakovljević, I.Šimić, G. Mendaš, Z. Sever Štrukil, S. Žužul, V. Glusščić, R. Godec, G. Pehnec, I. Bešlić, A. Milinković, S. Bakija Alempijević, M. Šala, M. Ogrizek, S. Frka, "Pollution levels and deposition processes of airborne organic pollutants over the central Adriatic area: Temporal variabilities and source identification," (in English), Mar. Pollut. Bull., Article vol. 172, p. 18, Nov 2021, Art no. 112873, doi: 10.1016/j.marpolbul.2021.112873.

B. Klun, U. Rozman, M. Ogrizek, and G. Kalčíková, "The first plastic produced, but the latest studied in microplastics research: The assessment of leaching, ecotoxicity and bioadhesion of Bakelite microplastics," Environ. Pollut., vol. 307, p. 119454, 2022/08/15/ 2022, doi: https://doi.org/10.1016/j.envpol.2022.119454.

M. Ogrizek, A. Kroflič, and M. Šala, "Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter," Trends Environ. Anal. Chem., vol. 33, p. e00155, 2022, doi: https://doi.org/10.1016/j.teac.2022.e00155.

M. Ogrizek, A. Kroflič, and M. Šala, "Determination of trace concentrations of simple phenols in ambient PM samples," Chemosphere, vol. 303, p. 135313, 2022/09/01/ 2022, doi: https://doi.org/10.1016/j.chemosphere.2022.135313.

M. Ogrizek, A. Gregorič, M. Ivančič, D. Contini, U. Skube, K. Vidović, M. Bele, M. Šala, M. Klanjšek Gunde, M. Rigler, E. Menart, A. Kroflič, "Characterization of fresh PM deposits on calcareous stone surfaces: Seasonality, source apportionment and soiling potential," Sci. Total Environ., vol. 856, p. 159012, 2023/01/15/ 2023, doi: https://doi.org/10.1016/j.scitotenv.2022.159012.

## Conference Paper

M. Ogrizek, M. Šala, and A. Kroflič, "Comparison of ICP-MS and LA-ICP-MS methods for the determination of elemental composition of PM10," in Abstract Book: 12th

International Conference on Carbonaceous Particles in the Atmosphere (ICCPA 2019), Vienna, Austria, 03. 04. - 06. 04. 2019.

M. Ogrizek, M. Šala, and A. Kroflič, "New method for the determination of elemental composition of PM on quartz fiber filters: LA-ICP-MS," in Abstract Book: European Aerosol Conference (EAC 2019), Gothenburg, Sweden, 25. 08. - 30. 08. 2019.

M. Ogrizek, M. Šala, and A. Kroflič, "Determination of metal content in PM deposited on quartz fibre filters with LA-ICPMS," in Abstract Book: European Aerosol Conference (EAC 2020), Aachen, Germany, 30. 08. - 04. 09. 2020.

A. Kroflič, K. Vidović, A. Gregorič, I. Drventić, M. Ogrizek, M. Bele, M. Rigler, M. Klanjšek Gunde, E. Menart, M. Šala, "Impacts of PM pollution on stone heritage," in Abstract Book: European Aerosol Conference (EAC 2021), virtual event, 20. 08. - 03. 09. 2021.

M. Ogrizek, A. Kroflič, and M. Šala, "Determination of phenols in PM by LC-MS," in Abstract Book: European Aerosol Conference (EAC 2021), virtual event, 30. 08. - 03. 09. 2021.

M. Ogrizek, M. Šala, and A. Kroflič, "Green method for determination of metal content in PM deposited on quartz fibre filter: LA-ICPMS," in Scientific Research Abstracts: IV International Conference on Atmospheric Dust (DUST 2021), Monopoli, Italy, 04. 10. - 07. 10. 2021, vol. 11.

M. Ogrizek, A. Kroflič, and M. Šala, "Elemental composition of PM deposited on quartz fiber filter by LA-ICPMS," in Conference booklet: European workshop on laser ablation (EWLA 2022), Bern, Switzerland, 12. 07. - 15. 07. 2022.

A. Kroflič, M. Ogrizek, A. Gregorič, U. Skube, I. Drventić, M. Bele, K. Vidović, M. Rigler, M. Klanjšek Gunde, M. Šala, E. Menart, "Source apportionment of PM deposits on stone surfaces," in Abstract Book: 111th International Aerosol Conference (IAC 2022), Athens, Greece, 04. 09. - 09. 09. 2022.

M. Ogrizek, A. Kroflič, and M. Šala, "Seasonal trends of nitrophenols and their precursors in ambient PM from Ljubljana," in Abstract Book: 11th International Aerosol Conference (IAC 2022), Athens, Greece, 04. 09. - 09. 09. 2022.

M. Šala, A. Kroflič, M. Ogrizek, S. Frka, M. Adamek, M. Hodošček, S. J. Blanksby, "Fragmentation patterns and mechanisms of environmentally important nitroaromatics studied by collision induced dissociation," in Abstract Book: 111th International Aerosol Conference (IAC 2022), Athens, Greece, 04. 07. - 09. 07. 2022.

M. Ogrizek, U. Skube, A. Gregorič, D. Contini, M. Bele, K. Vidović, M. Rigler, M. Šala, A. Kroflič, "Identification of air pollution sources in Ljubljana, Slovenia," in zbornik povzetkov: Slovenski kemijski dnevi 2022, Portorož, Slovenia, 21. 09. - 23. 09. 2022: Slovensko kemijsko društvo.

# Biography

Author of this thesis Monika Ogrizek started her higher education at the Biotechnical Faculty, University of Ljubljana, studying Biotechnology. She finished her academic bachelor's degree in 2012 with a thesis entitled "Selenium and cancer prevention". After that she continued the study of Biotechnology at the master's level. She performed her master's thesis under the supervision of Dr. Gregor Majdič at the Institute of Preclinical Sciences, Veterinary Faculty, where she investigated the influence of prenatal stress on aggressive and sexual behavior of male offspring. In 2017, she finished her master's degree with a thesis entitled "Effect of maternal stress in prenatal period on aggressive behavior of offspring in mice" and a first paper "Injections to pregnant mice produce prenatal stress that affects aggressive behavior in their adult male offspring" published in Hormones and Behavior. Between 2012 and 2014 she was also a recipient of a scholarship for talented students from the municipality of Maribor.

Along with her regular education, she was also active in the music field. She finished basic music education in subjects of piano and singing, and regularly participated in the top choirs (The Academic Choir Tone Tomšič, University of Ljubljana, and mix choir of Glasbena matica Ljubljana), with which she won many first prize awards in international choir competitions (*e.g.* Cork (Ireland), Spittal an der Drau (Austria), Arezzo (Italy), etc.) and gave a concert together with the top world singers (*e.g.* Elina Garanča, Krasmira Stojaniva, etc.).

In September 2018, she started working at the National Institute of Chemistry as a Young Researcher under the supervision of Dr. Martin Šala and Dr. Ana Kroflič, and enrolled in the doctoral study at the Jožef Stefan International Postgraduate School, Ecotechnologies program. During the doctoral study she successfully published six papers in high-ranking journals and presented her research to atmospheric and laser ablation communities in international conferences (*e.g.* EAC 2021, IAC 2022, EWLA 2022). In September 2022, she finished all her experiments and courses required for completing of doctoral study, which resulted in this dissertation.