

Guidance documents on measurements and  
modelling of novel air quality pollutants:

# PM (offline and online) speciation



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## **Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial Areas (RI-URBANS)**

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# Table of contents

ABBREVIATIONS .....	I
CHEMICAL SYMBOLS.....	II
<b>1. ABOUT THIS DOCUMENT.....</b>	<b>1</b>
<b>2. DEFINITION OF ATMOSPHERIC PARTICULATE MATTER, COMPONENTS AND SIZES.....</b>	<b>2</b>
<b>3. MEASUREMENT METHODS AND QUALITY CONTROL FOR PM SPECIATION.....</b>	<b>6</b>
3.1. OFFLINE PM SPECIATION .....	6
3.1.1. <i>State of harmonisation in the current air quality directive</i> .....	6
3.1.2. <i>Measurement of PM constituents</i> .....	8
3.2. ONLINE PM SPECIATION.....	21
3.2.1. <i>State of harmonisation in the current air quality directive</i> .....	21
3.2.2. <i>Measurement of the PM non-refractory components</i> .....	22
3.2.3. <i>Measurement of trace elements and metals</i> .....	34
3.3. DATA MANAGEMENT.....	44
<b>4. PAN-EUROPEAN OVERVIEW OF PM SPECIATION ACROSS URBAN ENVIRONMENTS .....</b>	<b>46</b>
4.1. OFFLINE PM SPECIATION.....	46
4.1.1. <i>Trace elements</i> .....	46
4.1.2. <i>Major PM10 components</i> .....	55
4.2. ONLINE PM SPECIATION: NON-REFRACTORY COMPOUNDS .....	59
4.2.1. <i>Introduction</i> .....	59
4.2.2. <i>Methodology</i> .....	60
4.2.3. <i>Levels of non-refractory-PM1 mass concentrations</i> .....	63
4.3. ONLINE PM SPECIATION OF TRACE ELEMENTS AND METALS .....	67
<b>5. RECOMMENDATIONS AND MAIN FINDINGS.....</b>	<b>67</b>
5.1. RECOMMENDATIONS ON MEASUREMENTS, QUALITY CONTROL AND DATA MANAGEMENT .....	67
5.1.1. <i>Offline PM speciation</i> .....	67
5.1.2. <i>Online PM speciation</i> .....	70
5.1.3. <i>Data management</i> .....	71
5.2. MAIN OBSERVATIONS REGARDING PM SPECIATION AT URBAN EUROPEAN SITES .....	72
5.2.1. <i>Offline PM speciation</i> .....	72
5.2.2. <i>Online PM speciation</i> .....	73
<b>6. REFERENCES .....</b>	<b>74</b>



## Abbreviations

<b>ACSM</b>	Aerosol chemical speciation monitor
<b>ACTRIS</b>	Aerosols, Clouds and Trace gases Research InfraStructure
<b>AMS</b>	Aerosol mass spectrometer
<b>AQ</b>	Air quality
<b>BC</b>	Black carbon
<b>BrC</b>	Brown carbon
<b>BSTFA</b>	N, O-Bis(trimethylsilyl)trifluoroacetamide, effective trimethylsilyl donor for derivatization of polar compounds to facilitate analysis by gas chromatography
<b>CAIS</b>	ACTRIS Canter for Aerosol in-Situ Measurements
<b>CEN</b>	European Committee for Standardization
<b>D</b>	Deliverable
<b>DCA</b>	Dicarboxylic acids
<b>DL</b>	Detection limit
<b>EAQP</b>	European Air Quality Portal from the European Environmental Agency (EEA)
<b>EBAS</b>	A database infrastructure developed and operated by Norwegian Institute for Air Research, with datasets from EMEP, ACTRIS, GAW, among others
<b>EC</b>	Elemental carbon
<b>ECAC</b>	ACTRIS European Canter for Aerosol Calibration and Characterization
<b>EBAS</b>	A database infrastructure developed and operated by Norwegian Institute for Air Research, with datasets from EMEP, ACTRIS, GAW, among others
<b>EEA</b>	European Environmental Agency
<b>EMEP</b>	European Monitoring and Evaluation Programme
<b>EN</b>	European standard
<b>EU</b>	European Union
<b>GC-FID</b>	Gas chromatography with flame ionization detection
<b>GC-MS</b>	Gas chromatography mass spectrometry
<b>HEPA</b>	High efficiency particulate air filter
<b>HPLC-FID</b>	High performance liquid chromatography with flame ionization detection
<b>HPLC-PAD</b>	High performance liquid chromatography with pulsed-amperometric detection
<b>HV</b>	High volume
<b>IC-PAD</b>	Ion chromatography with pulsed-amperometric detection
<b>ICP-MS</b>	Inductively coupled mass spectrometry
<b>ICP-OES</b>	Inductively coupled optical emission spectrometry
<b>IN</b>	Industry
<b>ISO</b>	International Organization for Stantardization
<b>LC-MS</b>	Liquid chromatography mass spectrometry
<b>LOD</b>	Limit of detection
<b>LOQ</b>	Limit of quantification
<b>LV</b>	Low volume
<b>M</b>	Milestone
<b>m/z</b>	Mass per charge
<b>MBTCA</b>	1,2,3-butanetricarboxylic acid
<b>MSA</b>	Methanesulphonic acid

<b>NAQD</b>	New European Air Quality Directive (formally adopted 14th October 2024)
<b>NF</b>	ACTRIS national facility
<b>NR</b>	Non-refractory
<b>NRT</b>	Near real time
<b>OA</b>	Organic aerosols
<b>OC</b>	Organic carbon
<b>OGTAC-CC</b>	ACTRIS Organic Tracers and Aerosol Constituents – Calibration Centre
<b>OM</b>	Organic matter
<b>PAH</b>	Polyaromatic hydrocarbon
<b>PIXE</b>	Particle-induced x-ray emission
<b>PM</b>	Particulate matter
<b>PM<sub>1</sub></b>	Mass concentration of particles <1 µm
<b>PM<sub>10</sub></b>	Mass concentration of particles <10 µm
<b>PM<sub>2.5</sub></b>	Mass concentration of particles <2.5 µm
<b>PM<sub>x</sub></b>	PM <sub>10</sub> , PM <sub>2.5</sub> and PM <sub>1</sub> , indistinctively
<b>PMF</b>	Positive Matrix Factorization, a receptor model for source apportionment
<b>PNC</b>	Particle number concentration
<b>PNSD</b>	Particle number size distribution
<b>POA</b>	Primary organic aerosol
<b>Q-ACSM</b>	Quadrupole aerosol chemical speciation monitor
<b>QA/QC</b>	Quality assurance and quality control
<b>RB</b>	Regional background
<b>RI-URBANS</b>	Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial Areas EU-project
<b>RIT</b>	Relative ion transmission correction
<b>SIA</b>	Secondary inorganic aerosol
<b>SOA</b>	Secondary organic aerosol
<b>SOP</b>	Standard operation procedure
<b>SUB</b>	Sub-urban background
<b>TE</b>	Trace elements
<b>ToF-ACSM</b>	Time of flight aerosol chemical speciation monitor
<b>TR</b>	Traffic
<b>TS</b>	Technical specifications
<b>UB</b>	Urban background
<b>UI</b>	Urban background industry
<b>UFP</b>	Ultrafine particles (meaning nanoparticles in this report)
<b>VLV</b>	Very low volume
<b>VOC</b>	Volatile organic compounds
<b>WHO</b>	World Health Organization
<b>XRF</b>	X-Ray fluorescence

## Chemical symbols

<b>Al</b>	Aluminum
<b>Al<sub>2</sub>O<sub>3</sub></b>	Aluminum oxide
<b>As</b>	Arsenic
<b>Ba</b>	Barium

<b>BaP</b>	Benzo(a)pyrene
<b>Be</b>	Beryllium
<b>Bi</b>	Bismuth
<b>Br</b>	Bromine
<b>Ca</b>	Calcium
<b>CaO</b>	Calcium oxide/Quicklime
<b>CaSO<sub>4</sub>2H<sub>2</sub>O</b>	Gypsum
<b>Cd</b>	Cadmium
<b>Cl</b>	Chlorine
<b>Co</b>	Cobolt
<b>CO</b>	Carbon monoxide
<b>CO<sub>2</sub></b>	Carbon dioxide
<b>Cr</b>	Chromium
<b>Cs</b>	Cesium
<b>Cu</b>	Copper
<b>Fe</b>	Iron
<b>Fe<sub>2</sub>O<sub>3</sub></b>	Iron oxide
<b>H<sub>2</sub>O<sub>2</sub></b>	Hydrogen peroxide
<b>HCl</b>	Hydrochloric acid
<b>HClO<sub>4</sub></b>	Perchloric acid
<b>Hf</b>	Hafnium
<b>HF</b>	Hydrofluoric acid
<b>Hg</b>	Mercury
<b>HNO<sub>3</sub></b>	Nitric acid
<b>HClO<sub>4</sub></b>	Perchloric acid
<b>K</b>	Potassium
<b>K<sub>2</sub>O</b>	Potassium oxide
<b>La</b>	Lanthanum
<b>Li</b>	Lithium
<b>Mg</b>	Magnesium
<b>MgO</b>	Magnesium oxide
<b>Mn</b>	Manganese
<b>Mo</b>	Molybdenum
<b>N</b>	Nitrogen
<b>Na</b>	Sodium
<b>Na<sub>2</sub>O</b>	Sodium oxide
<b>NaCl</b>	Sodium chloride
<b>NH<sub>3</sub></b>	Ammonia
<b>NH<sub>4</sub></b>	Ammonium
<b>NH<sub>4</sub>NO<sub>3</sub></b>	Ammonium nitrate
<b>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub></b>	Ammonium sulfate
<b>NH<sub>4</sub>Cl</b>	Ammonium chloride
<b>Ni</b>	Nickel
<b>NO<sub>3</sub></b>	Nitrate
<b>NO<sub>x</sub></b>	Nitrogen oxides (NO+NO <sub>2</sub> )
<b>O<sub>3</sub></b>	Ozone
<b>OH</b>	Hydroxyl radical

<b>P</b>	Phosphorus
<b>P<sub>2</sub>O<sub>5</sub></b>	Phosphorus pentoxide
<b>Pb</b>	Lead
<b>Rb</b>	Rubidium
<b>S</b>	Sulphur
<b>Sb</b>	Antimony
<b>Sc</b>	Scandium
<b>Se</b>	Selenium
<b>Si</b>	Silicon
<b>SiO<sub>2</sub></b>	Silicon dioxide
<b>Sn</b>	Tin
<b>SO<sub>2</sub></b>	Sulfur dioxide
<b>SO<sub>4</sub></b>	Sulfate
<b>Sr</b>	Strontium
<b>Th</b>	Thorium
<b>Ti</b>	Titanium
<b>TiO<sub>2</sub></b>	Titanium dioxide
<b>Tl</b>	Thallium
<b>U</b>	Uranium
<b>V</b>	Vanadium
<b>Y</b>	Yttrium
<b>Zn</b>	Zinc
<b>Zr</b>	Zirconium

# 1. ABOUT THIS DOCUMENT

This document summarises the guidance for speciation of atmospheric particulate matter (PM) elaborated in the "Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial Areas" (RI-URBANS) EU-project. This guidance is based on linking the atmospheric observation and analyses expertise from the "Aerosols, Clouds and Trace Gases Research InfraStructure" (ACTRIS), the urban air quality (AQ) observation capacities of the AQ monitoring networks (AQMNs) and RI-URBANS' scientific experts in AQ.

The new EU AQ Directive (NAQD, CEU, 2024) requires or recommends the analysis of specific PM<sub>10</sub> and PM<sub>2.5</sub> components, such as metals (arsenic, As; cadmium, Cd; nickel, Ni; lead, Pb), polyaromatic hydrocarbons (PAH), levoglucosan, elemental and organic carbon (EC and OC) as well as inorganic ions (sulphate, SO<sub>4</sub><sup>2-</sup>; nitrate, NO<sub>3</sub><sup>-</sup>; chloride Cl<sup>-</sup>; ammonium NH<sub>4</sub><sup>+</sup>; calcium, Ca<sup>2+</sup>; potassium, K<sup>+</sup>; magnesium, Mg<sup>2+</sup>; sodium, Na<sup>+</sup>). Protocols for specific sampling and analytical reference methods are supplied to this end in the NAQD, which shall be followed. Also, methods for which equivalence to the reference method is demonstrated may be used. However, in addition to these, for an advanced air quality assessment, including source apportionment, additional PM inorganic and organic components might be required (see next section).

PM speciation can be carried out by sampling (generally 24 h) and offline analyses in laboratories, but modern instrumentation also allows online PM speciation with < 1 h resolution that can be of high interest, for the above assessments but also to yield information to support short-term policy decisions, i.e., during pollution episodes. Both types of PM speciation methods are of interest and can be combined for advanced assessments. Both approaches are included in this guidance document.

In order to ensure that the information collected on PM speciation is comparable and sufficiently representative across the Union, it is important that standardised measurement techniques and common criteria are used for the assessment. The aim of this document is to facilitate the upscaling of measurement techniques for an advanced PM speciation within AQMNs. We provide an up-to-date summary of the harmonised methodologies related to PM speciation, summarise results from Pan-European observations, and provide concise recommendations on the determination of PM speciation in urban environments.

This is a RI-URBANS/ACTRIS guidance for this specific service tool that is part of the RI-URBANS deliverable D46 (D6.1) which, with the support for publication from AXA Research Fund, builds up the final dissemination D55 (D7.6). Any dissemination of results must indicate that it reflects only the author's view and that the European Commission is not responsible for any use that may be made of the information it contains.

## 2. DEFINITION OF ATMOSPHERIC PARTICULATE MATTER, COMPONENTS AND SIZES

Atmospheric suspended PM is defined as a complex mixture of solid and liquid particles suspended in the air (Mészáros, 1993). The terms “aerosol particles” are used as surrogate of PM. The complexity arises from i) the mix of origins, sizes and compositions of the solid and liquid particles, ii) the changes that particles might undergo after emission; and iii) possible sampling artefacts.

PM can be classified as primary and secondary, if it is emitted directly into the atmosphere, or formed into the atmosphere from gaseous precursors, respectively. PM can be also classified as natural or anthropogenic according to its emission sources.

PM particle sizes range from about 1 nm to around 100  $\mu\text{m}$ . The submicron fraction can be divided in the nucleation (1-20 nm), Aitken (20-100) and accumulation (100-1000 nm) modes. These are typically determined by particle number size distributions (PNSD) measurements using the number of particles/ $\text{cm}^3$  unit (Seinfeld and Pandis, 2016). Larger particles have historically been split in the fine (<2.5  $\mu\text{m}$ ) and coarse (2.5-10  $\mu\text{m}$ ) fractions. Current air quality standards fix limit values in  $\mu\text{g}/\text{m}^3$  for PM<sub>10</sub> and PM<sub>2.5</sub>, the mass concentration of particles with aerodynamic diameters less than 10  $\mu\text{m}$  and 2.5  $\mu\text{m}$  (50% cut-off), respectively. In scientific studies, PM<sub>1</sub> (diameter <1  $\mu\text{m}$ ) is also often measured and analysed.

The major constituents of PM are classically differentiated as follows (see Querol et al., 2001, and Alier et al., 2013, among many others):

- **Mineral matter** basically contains all the inorganic components of the Earth crust, including Si, Al, Fe, Ca, Na, Mg, K, Ti, P, Mn, etc... oxides and sulphides mostly, arising from wind production of suspended soil particles (desert dust, pavement erosion), construction and demolition works, in

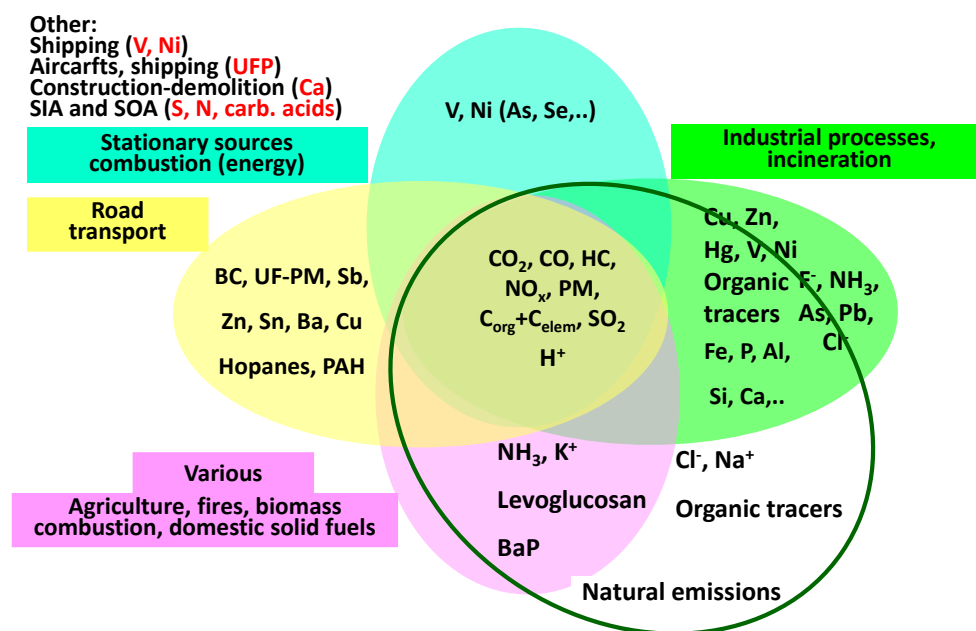
addition to some industrial emissions (such as the ceramic and cement industry). The maximum of mineral matter emissions is usually in the coarse mode.

- **Sea salt** is mostly composed of  $\text{Cl}^-$  and  $\text{Na}^+$  together with a fraction of  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$ . These have a dominant mode in the coarse fraction.
- **Organic matter (OM)** is a very complex mixture of organic compounds arising from primary combustion sources like e.g. hydrocarbons from vehicle exhaust emissions, levoglucosan and polyaromatic hydrocarbons from biomass burning, and many other compounds such as nicotine from smoking, azelaic acid from cooking, etc... In addition, organic matter includes secondary compounds such as carboxylic acids formed from oxidation of gaseous precursors in the atmosphere, and polymers of those. OM primarily occurs in the fine fraction.
- **Elemental carbon (EC)** is graphitic or amorphous carbon produced by incomplete combustion of fuels, from vehicles, biomass and coal burning. EC dominant mode is in the fine fraction.
- **Inorganic ions  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$**  constitute the secondary inorganic aerosol (**SIA**) from the atmospheric oxidation of gaseous  $\text{NO}_x$  and  $\text{SO}_2$ , respectively, followed by a reaction with gaseous  $\text{NH}_3$ . These occur as  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{HSO}_4$  and/or  $(\text{NH}_4)_2\text{SO}_4$  in the fine fractions of PM. The two first precursors arise from emission of combustion processes, while  $\text{NH}_3$  is primarily emitted from agriculture and farming (EEA, 2023a). Part of the  $\text{Cl}^-$  can contribute to SIA in the form of  $\text{NH}_4\text{Cl}$  in regions where anthropogenic HCl emissions are relevant. These have a dominant mode in the fine fraction. SIA can occur in the coarse mode where  $\text{NaNO}_3$  can form from nitric acid and sea salt.
- **Trace elements** comprise of a wide variety of elements (such as As, Cd, Ni, Pb, V, Zn) with different origin, toxicity and size distribution, present in the low concentration (in the  $\text{ng}/\text{m}^3$  range). The sources of trace elements include e.g. combustion, non-exhaust emissions (tyre dust, brake dust), exhaust emissions, and industrial emissions. These have a dominant role typically in the fine fraction, but those from traffic have a high load in the coarse mode. These and some organic compounds, such as PAHs are key components in PM speciation because some are carcinogenic and other have relevant toxic effects; but also, because these are key tracers for advanced source apportionment studies using receptor modelling.
- **Undetermined fraction** is the PM mass determined by gravimetry that is not accounted for by the sum of the concentrations of all the above PM components, because there are light atoms (typically H, N, O) whose contributions are not properly determined. For instance, crystallisation water accounts for 21% of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) molecular mass. PM bound water can still

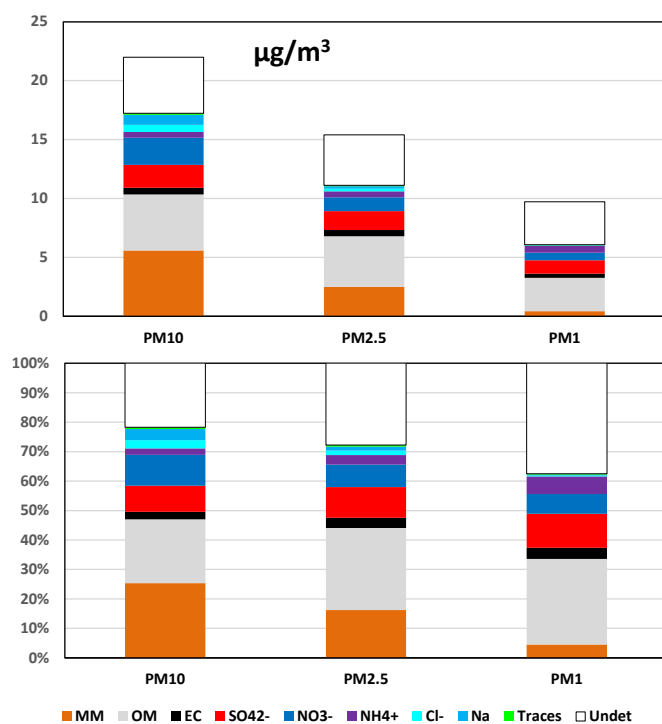
contribute significantly to the gravimetric mass if hygroscopic constituents are present, Furthermore, there might be heteroatoms that are not properly quantified in e.g. mineral matter.

A complete PM speciation analysis results in the determination of a large number of PM tracers of specific emission sources (Figure 2.1). Examples of relevant sources that can be traced by **inorganic tracers** include combustion processes (EC), non-exhaust (brake pads, brake disks, tyres, pavement) vehicle PM emissions (Ba, Cu, Fe, Mn, Sb, Sn, Zn, Zr; Harrison et al., 2021); soil dust (including road dust and desert dust) suspension (Al, Si, Ti, Ca; Querol et al., 2001), oil combustion including shipping and petrochemical plants (V, Ni, La; Amato et al., 2016), biomass burning (K; Amato et al., 2016), and a variety of industrial sources (As, Bi, Cd, Cr, Fe, Mn, Ni, P, Se, Tl; Amato et al., 2016), among others. Examples of relevant sources which can be traced by **organic tracers** are (van Drooge et al., 2022, and references therein): combustion sources (a variety of PAHs), biomass burning (galactosan, mannosan and levoglucosan), lubricant oils (hopanes), cigarette smoke (nicotine), soil dust (glucose), fungi (mannitol), plastics (phthalate esters), cooking (azelaic acid), secondary organic aerosols (a variety of carboxylic acids depending on the precursor VOC), among others.

As shown in Figure 2.2, the composition of PM10, PM2.5 and PM1 differ because different sources contribute to different particle sizes. Thus, the contribution of mineral matter and sea salt constituents tend to be larger in PM10 and smaller in PM1. In contrast, OC, EC and SIA relative proportions are generally larger in PM1 than in PM10.



**Figure 2.1.** PM tracers of specific emission sources that are widely used for source apportionment in receptor modelling.



**Figure 2.2.** Distribution of PM components (PM10, PM2.5 and PM1) at an urban background site in Barcelona in 2022, in  $\mu\text{g}/\text{m}^3$  (top) and % (below) to the respective PM mass concentration. MM, mineral matter; OM organic matter; EC, elemental carbon; Traces, sum of trace elements; Undet, undetermined mass concentration.

Exposure to high PM<sub>x</sub> (PM1, PM2.5 and PM10) concentrations are associated with increased respiratory and cardiovascular morbidity and premature cardiovascular mortality (WHO, 2021), with costs derived from these health impacts reaching 4.5% of global GDP (World Bank, 2016). Furthermore, PM can also have environmental impacts (on ecosystems and the climate, IPCC, 2021). Abating PM<sub>x</sub> is challenging because of the (i) mixed origin from different anthropogenic and natural sources, and (ii) the high proportion of secondary PM (Amato et al., 2016), requiring also the control of PM gaseous precursors.

In the last decades, a clear decrease in PM<sub>x</sub> concentrations in urban Europe has been observed as a consequence of the European, national, regional and local air quality policies implemented (EEA, 2023a). These include, e.g., the Directives on Industrial Emissions, on EURO standards for vehicles, regulations on Large and Medium Combustion Plants, as well as the implementation of Low Emission Zones (LEZ), congestion taxes, the increase of electric vehicles, among many others (EEA, 2022; Sicard et al., 2021; Turnock et al., 2016). However, the European Environment Agency (EEA 2023a) reported that 97% of the urban population of the EU-27 countries was still exposed to

ambient concentrations of PM<sub>2.5</sub> exceeding the respective guideline of WHO in 2021 (PM<sub>2.5</sub> air quality standard of 5 µg/m<sup>3</sup>, WHO, 2021).

Because the above significant PM abatement has been achieved by reducing primary PM and secondary inorganic PM precursor (such as SO<sub>2</sub> and NO<sub>x</sub>) emissions, a large proportion of PM<sub>2.5</sub> is nowadays made up of secondary organic aerosol (SOA) (in 't Veld et al., 2021), whose concentration is more difficult to reduce than that of primary PM.

Under this scenario, advanced PM speciation and subsequent source apportionment studies are key tools to i) validate emission inventories and subsequently evaluate the potential effects of various emission abatement scenarios, and ii) assess for cost-effectiveness the AQ measures to abate PM levels.

For further developments of WHO AQ Guidelines and EU AQ standards, long-term time series of PM speciation are needed on top of toxicological analyses to enable epidemiological studies aiming at identifying the PM components having the highest health impacts. As an example, significant associations of Mn, Zn and Ni with cardiovascular and/or respiratory hospitalisations were found at five south European cities (lag time 0-1 day) after normalisation to total PM levels (Basagaña et al., 2015).

## 3. MEASUREMENT METHODS AND QUALITY CONTROL FOR PM SPECIATION

### 3.1. Offline PM Speciation

#### 3.1.1. State of harmonisation in the current air quality directive

The EU Air Quality Directive sets limit values for mass concentration of PM<sub>10</sub>, PM<sub>2.5</sub> and Pb in PM<sub>10</sub>. In addition, it sets target values for annual concentrations of As, Cd, Ni, and benzo[a]pyrene until end of 2029, which will be transformed to limit values in 2030. Within the context of this EU AQ Directive, the European Committee for Standardization (CEN) has released the following European standards:

- EN12341:2023 'Ambient Air — Standard gravimetric measurement method for the determination of the PM<sub>10</sub> or PM<sub>2.5</sub> mass concentration of suspended particulate matter'.

- EN14902:2005 'Ambient air quality. Standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter'
- EN15549:2008 'Air quality. Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air'

In the absence of an EN standard method for other PAH compounds, the international standard ISO 12884, the European technical specification CEN/TS 16645:2014, or national standards may be used.

The EN15980:2011 specifies a method for the determination of the **bulk deposition (not concentration)** of benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBahA) and indeno[1,2,3-cd]pyrene (INP), which can be used in the framework of Directive 2004/107/EC.

The NAQD (CEU, 2024) includes the requirement of measuring PM2.5 chemical speciation at urban and rural supersites. Chemical characterisation of PM2.5 shall include at least:  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , OC and EC. These species do not have limit or target values. The reference methods are:

- EN16913:2017 'Ambient air - Standard method for measurement of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  in PM2.5 as deposited on filters'.
- EN16909:2017 'Ambient Air — Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters.'
- CEN/TS 18044:2024. 'Ambient air - Determination of the concentration of levoglucosan - Chromatographic method'.

In addition to the aforementioned CEN standards, ACTRIS – CAIS-ECAC (ACTRIS Centre for Aerosol in-Situ - European Centre for Aerosol Calibration and Characterization) provides recommendations for the determination of OC and EC in PM2.5 (<https://www.actris-ecac.eu/actris-gaw-recommendation-documents.html>) and the analysis of metals in PM (<https://www.actris-ecac.eu/pmc-elements.html>). Regarding water-soluble ions in PM, the Chemical Co-ordination Centre of EMEP (CCC) produced the "EMEP manual for sampling and chemical analysis" (EMEP/CCC-Report 1/95 Revision 1/2001; <https://projects.nilu.no/ccc/manual>) describing the methods recommended for sampling and chemical analysis for the EMEP measurement network, including the analysis of PM chemical components.

As stated in the NAQD (CEU, 2024), the main objectives of the measurements of mass concentration and chemical composition of PM<sub>2.5</sub> is “to ensure that adequate information is made available on levels in urban background and rural background locations. This information is essential to judge the enhanced levels in more polluted areas (such as urban background locations, air pollution hotspots, industry related locations, traffic related locations), assess the possible contribution from long-range transport of pollutants, support source apportionment analysis and for the understanding of specific pollutants such as particulate matter. It is also essential for the increased use of modelling applications also in urban areas”. It should be considered that the species listed as “mandatory” do not permit to perform suitable source apportionment studies. As concluded by Amato et al. (2024) in the framework of RI-URBANS, source apportionment studies require the analysis of tracers of specific sources. Thus, they recommended the determination of the concentrations in ambient air of EC, OC, major ions, major trace elements (including tracers of dust and various industrial, traffic and combustion sources, such as Al, Ca, Fe, Ni, V, Sb, Sn, Zn, among others), and biomass burning tracers (e.g., PAHs, sugars, carboxylic acids, etc). This enables identifying most of the main contributors to PM in Europe. For specific sources, they also recommended to measure methanesulphonic acid (MSA), oxalate, and sugar alcohols, among others.

Therefore, currently reference/harmonised methodologies do not exist for a complete chemical characterisation of PM<sub>10</sub> and/or PM<sub>2.5</sub> that would also enable performing comprehensive source apportionment studies. In the following chapter (3.1.2), we summarised the existing recommendations for sampling and analysis of specific PM constituents.

### 3.1.2. Measurement of PM constituents

#### 3.1.2.1. Sampling and collection media

Pm can be collected by filtration, by impaction and by electrostatic processes. Here we focus only on the filtration processes that are used in AQ standards. Then we exclude impactors, electrostatic precipitators, impingers and other sampling methods that are more used for scientific purposes.

Offline determination is based on the collection of a fraction of atmospheric PM on a substrate and its subsequent laboratory analysis. Frequently, the gravimetric determination of the mass concentration of the PM size fraction is conducted prior to the chemical analyses.

Offline analyses require the collection of atmospheric particles on specific substrates (mainly filters) by using a pump at a fixed flow rate during a predetermined period of time (usually 24 h). Samplers

are usually equipped with a sampling inlet, that permits to aerodynamically segregate the PM size fraction of interest (i.e., PM<sub>10</sub> or PM<sub>2.5</sub>).

The previous version of EN12341 (2014) specified a 24 h sampling period by using high (i.e., flow 30 m<sup>3</sup> h<sup>-1</sup>) or low volume samplers (1–2.3 m<sup>3</sup> h<sup>-1</sup>). The use of high-volume samplers permits the collection of sufficient PM mass for the determination of most PM components from a single filter sample. However, the current version of EN12341 (2023) describing the reference method for the sampling of PM<sub>10</sub> and PM<sub>2.5</sub> specifies the use of low volume samplers (flow 1–2.3 m<sup>3</sup> h<sup>-1</sup>), still for 24 h sampling periods. This can be a limitation given that the PM mass collected might be insufficient to perform a complete PM chemical characterisation when low volume samplers are used. In this case, it is usually needed to conduct simultaneous sampling using 2 or more low volume samplers equipped with different kind of filters depending on the subsequent chemical analyses.

Selection of the sampling substrate, i.e., generally filters, is key for the measurements of the different PM components (Table 3.1.1). Quartz fibre filters can be used with both high and low volume samplers. These filters are typically used for analysing of OC, EC and organic compounds. These can also be used for the sampling of ions and trace elements, if blank levels are low enough, and further analysed by Ion Chromatography (IC) and Inductively Coupled Plasma (ICP) spectrometric analyses. When quartz fibre filters and high-volume samplers are used, loaded filters are divided in fractions destined to different chemical analysis. The other filter types are not suitable for high volume sampling and for OC/EC analysis.

However, these filters are not appropriate for elemental analysis using X-Ray Fluorescence (XRF) or PIXE (Particle-Induced X-Ray Emission). PTFE (Teflon®) filters, used with low-volume samplers, are usually employed for subsequent analysis of major and trace elements, and ions. However, PTFE filters may get clogged in specific conditions when high concentration and/or high relative humidity occur. Nylon® filters are also recommended for analysis of ions, given the low negative artefact for NO<sub>3</sub><sup>-</sup> when using other media such as quartz filters (Schaap et al., 2004). Nevertheless, Nylon® filters are usually avoided in many field studies, since ion concentrations can be determined in leachates of the Teflon filter after the non-destructive XRF analysis. Thus, Nylon® filters are only recommended for specific studies of NO<sub>3</sub><sup>-</sup> in PM, especially in warm weathers. Glass fibre filters have also been used for PM sampling and chemical analyses but the high metal concentrations do not allow analysing many of them.

**Table 3.1.1.** Comparison of filter types (modified from Bergmans et al., 2022).

Filter type	Flow*	Weighing			Chemical characterisation			
		Hygros.	El charge	Mass	Elements	OC/EC	Organics	Ions
Glass fiber	HV, LV, VLV	(Low)	Low	High	N	(Y)	Y	Y
Quartz	HV, LV, VLV	Low	Low	High	Y*	Y	Y	Y
Teflon, PTFE	LV, VLV	Low	Low	Variable	Y	N	Y	Y
Polycarbonate	VLV	Low	(High)	Low	Y	N	N	Y
Cellulose esters	LV, VLV	High	(High)	(Low)	Y	N	N	N
PVC	LV, VLV	Low	High	Low	Y	N	N	Y
Nylon	LV, VLV	Low	(High)	Low	Artifacts	N	N	HNO <sub>3</sub>

\* High (HV; 30 m<sup>3</sup> h<sup>-1</sup>), Low (LV; 1 – 2.3 m<sup>3</sup> h<sup>-1</sup>), and Very-low (VLV; <10 L min<sup>-1</sup>) volume samplers. Hygros.: hygroscopicity; El charge: electrostatic charge.

### 3.1.2.2. Organic and elemental carbon

The concentrations of OC and EC in atmospheric PM collected on quartz fibre filters are typically measured using the thermal-optical offline analytical technique with an optical correction of charring. The most employed thermal protocols for the analysis of OC and EC in PM are the IMPROVE, NIOSH-like, and the EUSAAR-2 protocols, that reduces the possible positive bias in EC determination due to the incomplete evolution of OC (Cavalli et al., 2010). The optical correction for charring is generally performed via filter light transmission monitoring (TOT).

In order to assist EU Member States meeting the requirements of the 2008/50/EC Air Quality Directive, the European Commission issued the Mandate M/503 for the development of “standards concerning automated measurements of particle matter in ambient air and the measurement of its chemical composition (OC and EC, inorganic ions)”. A European Committee for Standardization (CEN) Working Group (WG 35) elaborated a European standard (EN16909:2017) for the measurement of airborne EC and OC in PM<sub>2.5</sub> (Karanasiou et al., 2015; Brown et al., 2017). The EUSAAR-2 thermal protocol (Cavalli et al., 2010) was adopted as the reference methodology for the determination of EC and OC in ambient PM<sub>2.5</sub> in EN16909. WG35 is currently evaluating the possibility to extend this standard to the determination of EC and OC in ambient PM<sub>10</sub> and proposed guidance to assess the equivalence of automated, (near) real-time methods used to measure OC and/or EC proxy with the European standard EN 16909.

The recommendation by ACTRIS for OC & EC analysis is to follow the EN16909:2017. ACTRIS guidelines highlighted the following points of EN16909 that are particularly important (<https://www.actris-ecac.eu/actris-gaw-recommendation-documents.html>):

- For off-line analyses: at least one field blank shall be collected every 14 samples.
- Samples should be stored at temperature below 5°C, if not analysed within 28 days from sampling.
- Instruments shall be regularly calibrated and TC (total carbon multi-point calibration) be conducted at least once every 12 months and after any major maintenance/modifications.
- The calibration should be checked at least during each measurement day, e.g., by the analysis of a sucrose spiked filter. Certified sucrose solution should be used for this.
- To verify the instrument long term stability, at least one punch of a large control filter shall be analysed on each measurement day or for each sample batch. Control filters can be obtained from ECAC on request.
- Temperature probe calibration shall be checked at least every 12 months and after any major maintenance/modification.
- Laser signal noise and drift shall be checked during instrument blank analysis on each measurement day or for each sample batch.

Urban and regional background supersites are also advised to follow the recommendations made to ACTRIS National Facilities (NFs), which include:

- The participation in the ACTRIS annual inter-laboratory comparison for the determination OC and EC loading ( $\mu\text{g}/\text{cm}^2$ ) in test filter samples is compulsory for ACTRIS sites.
- Except if technically not feasible (see next bullet point), a carbon monolith denuder shall be installed downstream of the sampling head and upstream of the filter holder. The dimension of a denuder should be such that the residence time in the denuder is about 1s. A denuder should be regenerated at least every 3 months or 2000  $\text{m}^3$ . The use of denuder is particularly important at remote or rural background sites where the relative contribution of positive sampling artifacts is higher.
- At observatories where the use of a denuder is not possible (e.g., extreme weather conditions, hi-vol sampling plus lack of technical solutions to have several denuders in parallel), positive artifacts shall be assessed across a whole year using one of the techniques described in e.g Watson et al. (2009).
- Field blanks shall be sampled for ca. 30 to 60 s (which is not specified in the EN16909 standard).

- The response of the instrument in the helium and in the helium/oxygen modes shall be checked on each measurement day (or sample batch) by injecting a fixed amount of calibration gas in the two analytical modes and should not differ by more than 5%.
- The laser correction coefficient shall be  $\leq 1$  but  $\geq 0.9$ .
- The transit time shall be regularly verified.
- The available integration options (such as the initial laser signal value determination, baseline, laser and detector slope corrections) leading to optimal determinations of the peak areas and split point shall be selected. Be sure to record the applied options in your meta data.

ACTRIS-ECAC also provide recommendations on thermal-optical on-line analysis of OC and EC using a semi-continuous field analyser in “Semi-continuous measurement of elemental carbon (EC) and organic carbon (OC)”, available at [www.actris-ecac.eu/pmc-oc-ec.html](http://www.actris-ecac.eu/pmc-oc-ec.html).

### 3.1.2.3. Ions, extraction and analysis

SIA account for a large fraction of PM. The determination of the concentration of the water-soluble inorganic ions (mainly  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) in PM is usually performed by IC analysis of a water leachate of a filter, or a fraction of the filter.

As requested by the European Commission Mandate M/503, was elaborated the European standard EN16913:2017 ‘Ambient air - Standard method for measurement of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  in  $\text{PM}_{2.5}$  as deposited on filters’.

The method is based on the water extraction of the filter followed by the analysis of the ions in the leachate by IC coupled to a conductivity detector. Alternatively, cations can be analysed by ICP-OES, except  $\text{NH}_4^+$ , which can also be analysed by photometry or conductometry. This procedure was initially devised for rural background sites but can be also used in other type of environments.

ACTRIS does not provide any guideline for the analysis of water-soluble ions in PM. The EMEP Manual (2001) provides some recommendations for sampling and analysis of ions in atmospheric particulate matter. The question is if it is mainly adapted to regional background stations.

### 3.1.2.4. Major and trace elements

The analysis of major and trace elements in PM is of high interest for tracing emission sources. Trace elements usually occur at very low concentrations (in the order of  $\text{ng m}^{-3}$  or lower) requiring robust analytical techniques with low detection limit. The most frequently used techniques can be grouped

into three main types: atomic spectrometric techniques, X-Ray methods, and activation analysis (Duarte et al., 2021). In recent years, the use of instrumental neutron activation analysis (INAA) has been considerably reduced, which is why it will not be considered in this section.

The most widely used atomic spectrometry-based techniques for PM chemical characterisation are the ICP Mass Spectrometry (ICP-MS) and ICP - Optical Emission Spectrometry (ICP-OES). Combination of ICP-MS and ICP-OES ensures very low detection and quantification limits (LODs and LOQs) in the order of ppb and ppt, in the solutions arising from the PM sample digestion, and allows to quickly determine the concentration of a wide range of elements, with precision and accuracy. Out of these two, ICP-MS is often the technique of choice due to lower LODs/LOQs and being one of the standard methods in the EU legislation (EN 14902:2005). The second method described in EN 14902:2005, graphite furnace atomic absorption spectrometry (GFAAS), is no longer commonly used as it is much slower and suffers from more interferences than ICP-MS. All these methods require a complete dissolution of the sample, which involves time-consuming and costly procedures using strong acids. Generally, the samples are digested with acids at high temperature and/or pressure. In CEN and NIOSH standards, the digestion is performed using microwave assisted acid digestion due to the smaller number of chemical reagents needed, the faster dissolution and the lower loss of volatile elements. Nevertheless, several methodologies have been proposed in the literature using different heating programs, digestion time, and acid mixtures (Duarte et al. 2021, and references therein). The acid digestion always carries an associated uncertainty being the percentage of recovery of the elements different to 100%. The standard EN 14902:2005 specifies a recovery requirement between 90 to 110% for Pb and Cd, and 85 to 115% for As and Ni. The selection of the acid mixture is a key issue since it must achieve the complete dissolution of the PM sample, keeping the elements stable in the final solution. Nitric acid ( $\text{HNO}_3$ ) or conventional *aqua regia* ( $\text{HNO}_3 + \text{HCl}$ ) are frequently used in routine analysis, often in combination with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Thus, according to EN14902 (2005), concentrations of Pb, Cd, As and Ni shall be determined by ICP-MS (or GFAAS) of a solution obtained by closed vessel microwave digestion using nitric acid and hydrogen peroxide. However, this acidic mixture does not allow complete digestion of silicon-containing compounds, and other specific minerals (e.g.  $\text{TiO}_2$ ) for which a combined hydrofluoric acid (HF) and  $\text{HNO}_3$  digestion is necessary. The use of HF is therefore necessary for a complete digestion, but as it is a more aggressive acid than, e.g.,  $\text{HNO}_3$  it can be dangerous and can affect the equipment if it is not completely evaporated and, in addition, it leads to the loss of B and Si during the HF evaporation. Thus, when using HF special safety procedures shall be implemented.

Querol et al. (2001) describe a protocol for PM digestion using HF:HNO<sub>3</sub>:HClO<sub>4</sub>, which has been widely used. For source apportionment analyses where road dust, non-exhaust vehicle PM, demolition/construction dust or desert dust is intended to be included, this type of digestion is required. Else, the use of X-Ray methods can be an alternative.

The use of X-Ray based techniques have steadily increased since the early 2000s. X-Ray-based methods such as PIXE and energy dispersive XRF are non-destructive techniques that involve minimal sample manipulation, and as such, offer a fast analysis technique where the chemical digestion step is skipped. Although XRF has higher LODs than PIXE, it requires less complex instrumentation, making it more affordable and easier to use.

ACTRIS guidelines provide some recommendations for multi-element analysis of PM filters, mainly based on XRF and/or PIXE techniques (<https://www.actris-ecac.eu/pmc-elements.html>):

- Filters used should have low concentrations of elements of interest. They should be clean, with low contamination, and thin to reduce the background in PIXE spectra and the contribution of residual bulk contaminants.
- The sampling should produce as much homogeneous aerosol deposit as possible.
- After the sampling the filters should be stored in Petri slides, in order to avoid that the filter surface with the aerosol deposit on it could get in contact with materials that could result in loss of the aerosol deposit or in contamination.
- The use of small Ziplock plastic bags or wrapped aluminium foils should be avoided.

XRF techniques can only be applied when PM samples are collected on Teflon filters, which requires the use of low-volume samplers. This technique, unlike ICP-based methods, allows direct determination of Si. However, the detection limits of some tracers of interest to study the contribution of sources, such as As, Cd, Sb, Se, Sn, among others, can be considered (too) high. On the contrary, analysis by ICP-MS and ICP-OES requires acid digestion, are time consuming and more expensive, but LODs are very good for more than 50 elements.

#### *3.1.2.5. Organic markers, extraction and analysis*

Organic aerosol (OA) is a highly dynamic and complex heterogeneous mixture of organic compounds, that typically represents between 20 and 80% of the total atmospheric PM (Putaud et al., 2004; Jimenez et al., 2009; Kanakidou et al., 2005). Given their association with specific emission sources, some primary organic compounds are used as molecular markers to identify the presence

and contributions of the different sources to PM (Schauer et al., 2007). On the contrary, secondary organic aerosol (SOA) mainly originates from the oxidation of volatile organic compounds (VOC) in the presence of atmospheric oxidants such as nitrate (NO<sub>3</sub>), ozone (O<sub>3</sub>) or hydroxyl radicals (OH) (Atkinson et al., 2000, Palm et al., 2018; Robinson et al., 2007; Srivastava et al 2022).

This section reviews the analytical techniques for the analysis of molecular organic markers in ambient air PM filter samples, collected generally during 24 hours with the use of low and high-volume samplers with particle cut-off of 10 µm, 2.5 µm, or less than 1 µm (aerodynamic diameter). Some of these marker compounds, such as polycyclic aromatic hydrocarbons (PAHs), are air pollutants that cause adverse effects on human health and the environment, while many others are less toxic but are directly related to an emission source, such as anhydro-monosaccharides from biomass burning (Medeiros and Simoneit, 2007). On the other hand, secondary organic aerosol (SOA) compounds are formed from reactions of both anthropogenic and biogenic volatile organic compounds (VOC) and are mainly composed of oxygenated organic compounds (Hallquist et al., 2009). Overall, the knowledge about sources, fate and mutual interaction of gas phase and aerosol organic compounds, which are estimated to be between 10 000 and 100 000 different compounds, has improved over the past decades through scientific research. For example, secondary organic molecular marker compounds, such as 2-methyltetrols, are now being recognised and identified as SOA makers of isoprene (Claeys and Maenhaut, 2023). These compounds, and many other SOA compounds, do not fulfil the strict definition of 'tracer' compounds, since SOA compounds do not move through the atmosphere from a known source, but instead are being formed through photo-chemical gas-phase reactions. In fact, although many of the primary organic aerosol (POA) compounds resist certain degree of degradation, they are all vulnerable to transition through reactions. Therefore, the term 'marker' compound is more appropriate than 'tracer'.

The source apportionment of the OA is a challenging task, due to the large variety of VOC and POA emission sources, large quantity of organic compounds, as well as the large number of variables influencing the fate of these organic compounds during atmospheric transport, such as meteorological conditions. Important emission sources involve combustion (including vehicle exhaust and biomass burning), cooking activities, industries, and agriculture, but also resuspension of soil-dust, and plant detritus, with more or less influence from anthropogenic or biogenic origin, depending on the land-use (Schauer et al., 2007; van Drooge and Grimalt, 2015).

Over the past decades, the research on molecular organic markers with off-line filter techniques in combination with detection techniques, such as gas chromatography–mass spectrometry (GC-MS) and liquid-chromatography-MS, allowed the identification and quantification of a wide range of organic compounds, despite the fact that these techniques generally cover a very small fraction (often <5 %) of the total organic aerosol mass. Nevertheless, this relatively small number of identified marker compounds can be used as an input for chemometric methods, such as Positive Matrix Factorization (PMF), with the aim to re-construct the contributions from different sources or processes (Amato, 2024).

For the analysis of PM organic constituents, an overall standardised methodology is lacking, and only exists for PAHs, and in specific for benzo[a]pyrene. The sampling, detection, and quantification of PAH compounds in PM is performed by passing air volumes through a filter during several hours (typically 24 h), subsequent extraction of these filters by organic solvents, clean the system between samples, and PAH determination by gas or liquid column chromatography coupled to mass spectrometry, or fluorescence detection systems (EN15549:2008, CEN/TS 16645:2014, ISO 12884:2000, USEPA TO-13A, ISO 16362:2005).

The mass concentration of particulate organic tracers is an additional chemical variable within the ACTRIS aerosol in-situ framework, supported and serviced by the Organic Tracers and Aerosol Constituents – Calibration Centre (OGTAC-CC) as one unit within the CAIS-ECAC (Centre for Aerosol In-Situ – European Centre for Aerosol Calibration and Characterization) consortium. OGTAC-CC was originally established within the former Eurochamp project and is now in its implementation phase (funded by ACTRIS-D) as calibration centre for the offline determination of particulate organic marker compounds collected on filters (substrates). Besides training of operators and scientists in good practice related to aerosol particle filter sampling, sample transport and storage, sample preparation until data analysis, the current focus within the implementation phase is to set up technical requirements and measurement guidelines as the base to develop standard operating procedures (SOP) for different modules of target compounds, e.g., a biomass burning module containing levoglucosan, mannosan and galactosan. Method evaluation and QA/QC is performed by interlaboratory comparisons. OGTAC-CC established regular community meetings to foster the harmonisation of analytical techniques for the analysis of organic markers.

It is important to note again that there is CEN/TS 18044:2024 for levoglucosan measurements that shall be followed.

Despite the existing variety of analytical techniques, the obtained results should comply equivalence within a low range of uncertainty, as it does for PAHs. For these classical air pollutants, or those compounds that are directly related to source emissions (POA markers), analytical standards are commercially available, which facilitate the optimisation of analytical methods and the equivalence studies among the methodologies. The study of SOA markers is more challenging since these analytical standards are often not available, and their determination and quantification is performed indirectly through the analysis of other compounds. Moreover, the determination of specific compounds may be compromising the analysis of compounds with different physico-chemical properties, such as volatility or polarity. Ideally, standardised methodologies for molecular organic markers should cover a wide range of these properties (Fontal et al., 2015). The selection of solvents to extract the target compounds from the filters is a first step in this methodology, while further steps in the procedure, such as extraction, purification and compound derivatisation, as well as analytical detection techniques, adding compromising conditions to the final list of potential molecular organic markers in PM to be quantified.

This chapter reviews the existing methodologies and proposes strategies for those organic markers that lack equivalent methodologies. The list is not conclusive, since many more markers will be identified in the future.

The following primary organic aerosol markers are discussed in this chapter:

- Polycyclic aromatic hydrocarbons: PAHs are toxic components and primary products of incomplete combustion of fossil fuels and biomass (Galarneau, 2008; van Drooge et al., 2023). Benzo[a]pyrene is the only organic compound in atmospheric PM that has an annual target value of 1 ng/m<sup>3</sup> (limit value of 1.0 ng/m<sup>3</sup> after 2029) in the European AQ directive (EU, 2024 and EU, 2008).
- Anhydro-monosaccharides: Levoglucosan, galactosan and mannosan. They are monosaccharide anhydrides generated by thermal alteration of cellulose and hemi-cellulose and are emitted in large quantities (up to 10 % of mass) during biomass burning (Medeiros and Simoneit, 2007; Fine et al., 2004). In areas with large contribution of biomass burning emission, these anhydro-monosaccharides are highly correlated with PAHs (Jaen et al., 2021). In the NAQD, measurement of levoglucosan is recommended at supersites.
- Saccharides: alpha- and beta-glucose are primary monosaccharides that are abundant in vegetation and soils, and often related to soil-dust resuspension or thermal stripping of vegetation

during biomass burning (Medeiros and Simoneit, 2007), and therefore often appearing in the coarse fraction of aerosols (van Drooge and Grimalt, 2015). On the other hand, mannitol, sorbitol and arabitol, are alcohol-sugars that are often associated with fungal spores, besides plant debris, and pollen, with contributions from various natural and anthropogenic processes (Samaké et al., 2019a, 2019b).

In addition, the following secondary organic aerosol markers are discussed in this chapter:

- **Dicarboxylic acids (DCA)**, hydroxy-DCA and aromatic-DCA, such as succinic acid, azelaic acid, malic acid and phthalic acid, can be emitted from various primary sources (mobile emission, meat cooking, etc.) although atmospheric photo-chemical formation is their main source (Alier et al., 2013; Heald et al., 2010; Paulot et al., 2011).
- **Cis-pinonic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)**. They have been identified in aerosols and related to the photo-chemical oxidation of biogenic volatile compounds such as  $\alpha$ -pinene (Claeys et al., 2007). 3-MBTCA is formed by OH initiated oxidation of cis-pinonic acid (Kubatova et al., 2000).
- **2-methylglyceric acid and polyols, such as C5 alkene triols and 2-methyltetrols**. They have been related to isoprene oxidation (Claeys et al., 2004; Claeys and Maenhaut, 2023; Hallquist et al., 2009; Szmigielski et al., 2007), a major volatile organic compound emitted from land vegetation.

See Table 3.1.2. on the molecular organic aerosol markers in atmospheric particulate matter for emission sources and SOA processing, and their analytical procedures and references.

### 3.1.2.6. *Indirect determinations and mass closure*

The combination of the aforementioned techniques enables the determination of the concentration and contribution of all PM components. To reconstruct the PM mass concentrations and check the mass closure, we can estimate the contribution of the defined major PM components as follows:

**Dust or mineral matter** mass concentration can be estimated from the typical dust elements, such as Si, Al, Ti, P, Ca, Fe, Mg, Mn and fractions of Na and K. The total mineral dust concentration can be determined by addition of the concentrations of all mineral related elements expressed as oxides, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O. Part of these elements may have a marine origin (Na, K, Ca, Mg) or can be associated to other natural or anthropogenic sources such as biomass combustion (K).

**Table 3.1.2.** Molecular organic aerosol markers in atmospheric particulate matter for emission sources and SOA processing, and their analytical procedures and references.

	Group	Source/Precursors	Marker compounds	Solvent	Separation /Detection	Refs.	
POA	*PAH	Traffic exhaust Biomass burning Combustion	benz[a]anthracene benzo[b]fluoranthene benzo[k]fluoranthene <b>benzo[a]pyrene</b> benzo[ghi]perylene chrysene inden[123cd]pyrene retene	Dichloromethane Hexane Acetone Toluene	GC-MS GC-MS/MS GC-FID HPLC-FID HPLC-FLD LC-MS GCxGC-TOFMS TD-GC-GC-MS	CEN/ TS 16645:2014; EN 15549:2008; EPA TO-13A, 1999; Fontal et al., 2015; ISO 12884:2000; ISO 16362:2005; Schauer et al., 2007; van Drooge et al., 2023; Van Drooge & Grimalt, 2015)	
	Hopanes	Traffic	17a(H)21β(H)-30-norhopane 17a(H)21β(H)-hopane		GC-MS GC-FID	(Alier et al., 2013; Schauer et al., 2007; Van Drooge and Grimalt, 2015)	
	n-alkanes	Combustion	nC20 – nC25			GC-MS	(Alier et al., 2013; Schauer et al., 2007; Van Drooge and Grimalt, 2015)
		Vegetation detritus Soil dust	nC27, nC29, nC31			GC-FID	
Saccharides	Biomass burning	levoglucosan, mannosan, galactosan		Dichloromethane Methanol	GC-MS (BSTFA)	(CEN/TS 18044:2024; Fine et al., 2004; Fontal et al., 2015; Medeiros & Simoneit, 2007; Samaké, Jaffrezo, Favez, Weber, Jacob, Albinet, et al., 2019; Van Drooge & Grimalt, 2015)	
	Soil dust Vegetation detritus Fungal spores	glucose, arabitol, mannitol, sorbitol		Water	GC-MS/MS (BSTFA) LC-MS HPLC-PAD IC-PAD TD-GC-GC-MS		
SOA	Acids and polyols	Biogenic and anthropogenic VOCs	succinic acid, glutaric acid, malic acid	Dichloromethane Methanol Water	GC-MS (BSTFA) GC-MS/MS (BSTFA)	(Alier et al., 2013; Claeys et al., 2007, 2004; Claeys and Maenhaut, 2021; Fine et al., 2004; Heald et al., 2010; Kubátová et al., 2000; Medeiros and Simoneit, 2007; Palm et al., 2018; Paulot et al., 2011)	
		Naphthalene (combustion)	phthalic acid	Acetone	LC-MS		
		Oleic acid (food cooking)	azelaic acid		HPLC-PAD IC-PAD		
		Isoprene (vascular plants)	2-methylglyceric acid, C5 triols, 2-methylthreitol, 2-methylerythritol				
		Alpha-pinene (pine forests)	cis-pinonic acid, 3-hydroxyglutaric acid, **MBTCA				

\*PAH: polycyclic aromatic hydrocarbons; \*\*MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

The mineral fraction of these elements can be estimated from the concentrations of eminent mineral elements, such as Al or Ti, considering the usual proportions in Earth's crust (Lide, 2005), or in desert dust (Moreno et al., 2006; Alastuey et al., 2016) The dust fraction can also be estimated discounting the marine fraction (see next) from the bulk concentration (Alastuey et al., 2016).

**Sea salt:** the major constituents of sea salt are Cl, Na, Mg, Ca, K and sulphate. Their concentrations in sea water are well known (Lide, 2005), and therefore it is possible to estimate the marine contribution to their PM concentrations once we know the concentration of one of these elements coming exclusively from sea-spray. In marine-influenced and background areas, Cl<sup>-</sup> has a major marine origin, therefore the marine fraction of each element could be estimated from Cl<sup>-</sup> concentrations. However, this method may result in an underestimation of the marine aerosol due to the interaction of NaCl with acidic species resulting in the formation of HCl or NH<sub>4</sub>Cl, which may be volatilised in the atmosphere (Harrison and Pio, 1983). The sea-salt contribution to Cl, Na, Mg, Ca, K and S can be estimated for each element prior to estimating the mineral load.

**Organic matter (OM)** mass concentration can roughly be estimated from OC, or calculated from aerosol mass spectrometry measurements (AMS). Thus, AMS determines the mass concentration of ions arising from electro-thermal ionisation of organic species, and this mass accounts not only for OC but for O and H. By obtaining the sum of all the mass concentration of the organic ions, the total organic aerosols, equivalent to OM can be determined. If OC is measured (by thermal-optical technique) simultaneously the OM/OC ratio can be obtained. Subsequently this OM can be estimated from OC in filters by applying this local OM/OC ratio. If this is not possible literature OM/OC can be used, which vary from 1.3 to 2.4 (Malm et al., 2020 and references therein). Lower OM/OC ratios are usually found for less aged aerosols, generally more abundant at urban sites and in winter, compared to rural sites and summer periods (Malm et al., 2011). Thus, the OM/OC ratios usually applied at urban and rural sites are 1.3-1.8 and 1.8-2.4, respectively. Recent studies evidenced an increasing trend in OM/OC ratios (Malm et al., 2020).

The total PM mass concentration determined by chemical speciation will be the sum of the concentrations of the mineral dust, marine aerosol, EC, OM and SIA (as the sum of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>). The undetermined fraction is the difference between the PM mass determined by gravimetry and the total mass determined by chemical speciation. This undetermined mass can be related to PM-bound water (from hygroscopicity, crystallisation and formation) that is not properly determined, and to the underestimation of OM.

## 3.2. Online PM speciation

This section reviews the measurement methods for online PM speciation with <1 h resolution that can be of high interest to yield information to support and assess short-term AQ management decisions. There is a number of instruments available for the online determination of different PM components. Here we focus on the two most commonly used currently. The Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) is the most widely used instrument for measuring non-refractory PM<sub>1</sub> (NR-PM1) components, including various types of organic aerosols. The main commercially available instrument that provides real-time analyses of trace elements and metals is the Xact 625i Ambient Metals Monitor, developed by Cooper Environmental Services (Sailbri Cooper Inc., Tigard, OR, USA).

There are also some instruments available for online determination of concentrations of carbonaceous aerosols in PM. This is of increasing importance given that carbonaceous (OC + EC) matter is usually the largest contributor to PM<sub>2.5</sub> mass. As aforementioned (section 3.1), online thermal-optical measurements of OC and EC can be performed by using the semi-continuous OCEC Sunset analyser (Sunset Inc.). There is another instrument that allows OC and EC determination the Desert Research Laboratory

### 3.2.1. State of harmonisation in the current air quality directive

There are currently no CEN standards for online measurements of aerosol constituents.

Regarding online measurements on NR-PM1 using ACSM, other initiatives such as the COST-COLOSSAL Action have produced guidelines (<https://www.cost.eu/actions/CA16109/>). Standard Operating Procedures (SOP) documents both for Q-ACSM and ToF-ACSM produced during the COST-COLOSSAL Action which presents indications for the installation settings, servicing, checks, maintenance, quality assurance and quality control (QA/QC), and diagnostics are available (COST-COLOSSAL (2021), COST-COLOSSAL/ACTRIS (2022)). These guidelines are adopted by ACTRIS. Also, some publications describing this instrumentation and performing intercomparisons can be found on the aforementioned webpage. While user guides are available at [support.aerodyne.com](http://support.aerodyne.com), further recommendations for operation and data processing can be found at the ACTRIS-ECAC website (<https://www.actris-ecac.eu/pmc-non-refractory-organics-and-inorganics.html>).

As regards to real-time analysis of trace elements and metals, no guidelines have so far been produced. However, there is an increasing scientific interest in high time resolution XRF

instrumentation for atmospheric aerosol measurements in Europe. Currently there are three online XRF instruments available and users are encouraged to refer to the user guides and manuals for detailed information about the operation of the instrument. These are provided by the manufacturer Cooper Environmental at <https://cooperenvironmental.freshdesk.com> for the Xact 625i, Skyray Instrument Ltd., China for the Atmospheric Heavy Metals On-line Analyser EHM-X100 () and Horiba Ltd., Japan for the Particulate Monitor with X-Ray Fluorescence PX-375.

The Imperial College London (ICL) and the Paul Scherrer Institute (PSI), which were amongst the first users of such instrumentation, established in 2022 the Working Group “ROXI” (Real-time Online XRF Instruments). “ROXI” currently comprises over 70 users from 14 countries around Europe. Since June 2023, the group has been established as an ACTRIS Working Group on Online metal analysis by the NF Forum Programme Committee (<https://www.actris.eu/facilities/national-facilities/forum>). The purpose of “ROXI” WG is to draft operational (SOP, data treatment, QA/QC and reporting data/uncertainties) and source apportionment recommendations. Currently the group only has Xact 625i users as this is the only regularly used online instrumentation model. At present, the group is supported by the Xact manufacturer.

### 3.2.2. Measurement of the PM non-refractory components

In aerosol science, non-refractory (NR) aerosol comprises all the compounds that flash-vaporise at 600°C, since this is the typical temperature at which some of the most aerosol mass spectrometers vaporise aerosol. Among the aforementioned components, only the SIA, comprising of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and the OA fall under this NR definition.

Currently, the most commonly used instrument used for online NR- $\text{PM}_{10}$  speciation measurements is produced by Aerodyne Inc., Billerica, MA, USA, produces devices. However, new developments, such as Ionicon, with Fusion system, could be the first alternative. The most used instrument for long-term monitoring is the ACSM, based on the continuous acquisition of the mass spectra of the main NR chemical species within the submicron PM fraction in continuously sampled air. The ACSM is a more robust and simplified version of the Aerosol Mass Spectrometer (AMS), being hence more suitable for long-term unattended deployment and routine monitoring applications. This instrument provides the ambient concentration of OA,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$ . Different sources of OA can be identified by applying the positive matrix factorisation (PMF) receptor model to the organic mass spectra.

The Aerodyne company offers Quadrupole-Aerosol Chemical Speciation Monitor (Q-ACSM) and Time of Flight-ACSM (ToF-ACSM). The Q-ACSM is usually the most widely used because it is less expensive and easier to use. The ToF-ACSM, reaching lower detection limits, is more suitable for more pristine environments. Recently, a new version of the ToF-ACSM, the ToF-ACSM X, was launched, with an improved elemental analysis compared to the Q and ToF, which enables the calculation of O:C and H:C ratios. The ACSM can be configured with either PM1 or PM2.5 aerodynamic lens, however, the latter option requires a capture vaporiser to avoid particle losses.

Continuous measurements of inorganic species can also be achieved using ion chromatography downstream of Particle-Into-Liquid Sampler (PILS) or Steam Jet Aerosol Collector (SJAC) systems. These are designed to collect particles in an airstream by condensing water vapour on them to form droplets that can be collected by impaction. The solution can be analysed for inorganic ions, small organic acids and water-soluble organic carbon (WSOC). In both cases, the removal or subtraction of gaseous inorganic species should be achieved to obtain proper measurements of the particulate phase. There are near-real-time (NRT) instruments that allow the determination of soluble ions of PM and some gaseous species. Among these, the Monitor for AeRosols & Gases in ambient Air (MARGA, Metrohm AG) and the URG Mass Aerosol Speciation Sampler (MASS), developed by University Research Glassware, consist of a wet denuder, a steam jet aerosol collector and an IC, and can be used to determine inorganic gaseous and particulate compounds in ambient air. These instruments enable determining in NRT the concentrations of soluble anions and cations, as well as gaseous species such as NH<sub>3</sub>, among others. However, unlike the ACSM, these instruments do not permit to simultaneously measure all the NR-PM1 species.

### 3.2.2.1. *Sampling and conditioning*

#### *Sampling*

The ACSM has an internal sample flow rate of around 0.1 L min<sup>-1</sup>, which is fixed by a critical orifice at the inlet of the vacuum chamber. This flow rate is too low to ensure accurate sampling of ambient particles through a sampling line that is several metres long. Therefore, the ACSM shall sample from a primary flow, whose flow rate is higher to reduce the air residence time in the sampling line, and consequently, particle loss through diffusion. It is recommended to use a sampling line made of a conductive material in order to reduce particle losses. Stainless steel is preferred due to potential oxidation of copper on the long-term (i.e., several years). The length of the sample lines should be minimised. An external sampling pump must be used to get the flow in the sampling system at the

recommended flow of 3 L min<sup>-1</sup>. The COLOSSAL guidelines report that *“the split from the ½ inch sampling line to the 1/8 inch inlet tubing at the ACSM inlet is designed to be isokinetic at 3 L min<sup>-1</sup>”*, therefore, both the air flow and the diameter of the sampling line are actually fixed. The sample flow should be continuously recorded to monitor its stability. It is recommended to cut-off coarse particles from the primary air flow using a cyclone. The cyclone 50% cut-off diameter should be about 2.5 µm and 4 µm for ACSMs measuring the PM1 and PM2.5 size fractions, respectively. The PM2.5 cyclone recommended by the manufacturer (URG-2000-30ED) is compatible with a PM1 ACSM primary sample flow rate of 3 L min<sup>-1</sup>.

### *Drying*

The ACSM sampling line system should routinely be maintained at a relative humidity between 20% and 60%. The main cause for the need of a drainage system is the impact of aerosol water content to the accuracy of the collection efficiency (CE) determination. Nafion® membrane dryers are recommended over dryers with silica beads as they require less maintenance. The dryer must have a metallic casing to reduce the loss of charged particles.

The manufacturer offers a Nafion® dryer which enables all of its variables (i.e. relative humidity, temperature, dryer’s inlet pressure, dryer inlet/outlet differential pressure, and dryer sheath pressure) to be recorded. It functions with a pump which also controls the sample flow (section 3.1.3) as well as the reverse flow in the dryer. It is recommended to compare the humidity sensors on this dryer with a reference sensor annually.

To avoid condensation in the sample line ahead of the dryer, especially when hot / humid air enters an air-conditioned room, the distance between the dryer and the outside should be minimised and/or well insulated. Finally, it is important to ensure that there is no leak in the sampling system. This can be checked by placing a HEPA filter at the inlet of the sampling line and/or by verifying the correspondence of the flow measured on both sides of the sampling line.

### *Particle losses*

As with other instruments that measure the characteristics of aerosols, the losses in the sampling system should be evaluated, considering parameters such as the length and diameter of the line, the sample flow, the presence of bends, a dryer, etc. These losses can be modelled with Wavemetrics IGOR Pro using the PLC tool (free download available at: <http://www.mpch-mainz.mpg.de/~drewnick/PLC/>). Nevertheless, losses in the lines are minimised by following the

recommendations described above, specifically avoiding bends in the sampling line, ensuring a straight laminar flow in the line and using metallic tubing.

### *Sampling frequency*

Usually, the Q-ACSM is run in ambient air with a time resolution of about 30 min (corresponding to 28 sets of 1 open followed by 1 closed measurement scan, at 200 ms/amu). This time resolution may be set to approximately 1 h at remote sites displaying very low concentrations. Conversely, a 15 min time resolution (or better) may be better suited when substantial emissions from local sources are expected. It is important to note that for AQMNs, it is important to know that measurement time-base/period cannot be strictly the same from one sample to another one. Thus, in the end, data has to be weighted for their actual measurement duration (and not simply averaged) to get them on their usual time-base.

For the ToF-ACSM, due to its more potent detector, the time and spectral resolution are enhanced with respect to the Q-ACSM predecessor. Data is acquired every 40 s, with 20 s in filter and 20 s in sample modes. Multiple sets of 40 s are averaged together to improve the stability of the measurements and decrease the size of the data files. This data compilation results in NR-PM1 measurements every 10 minutes in the standard configuration, which, as aforementioned, can be modified to elongate or shorten the measurement time resolution.

### Performance criteria and test procedures for the sampling and conditioning system

The performance criteria for the sampling system which shall be met in the performance tests, should also be specified. The instrument must enable the following variables to be recorded in the highest time resolution feasible for posterior QA/QC checks.

- Date and end time of each reported concentration, with UTC recommended. It's important to keep the PC/laptop system as UTC as well in this case. The local time shall be manually corrected based on the UTC afterwards.
- Inlet pressure, inlet flow, air beam signal intensity, vaporiser temperature, instrument voltages, and other metadata essential for posterior analysis.
- Intensity of the counts of the detector per each species.
- Turbopumps temperature, power, frequency, status and MD1 power. Retrieved by the pump's software for the Q-ACSM and by the Acquility software for the ToF-ACSM.

- Input and output relative humidity of the sampled air before and after passing through the dryer. Retrieved by the dryer software every five minutes.

Also, the requirements for adequate ACSM deployment and maintenance are:

- The ACSM needs to be installed in an air-conditioned environment to prevent the turbo pumps or the Prisma detector from failing due to overheating (to be maintained below 25°).
- Avoid direct flow of the AC system onto the instrument or sampling line.
- The ACSM should be connected to the Internet to allow remote access control of the instrument (e. g. via TeamViewer/Anydesk) and to collect data.
- The Q-ACSM requires 300W of power and operates on 85-264 VAC, 47-63 Hz, while the ToF-ACSM requires 350W of power, and operates 90-260 VAC, 50-60 Hz.
- An inverter (for example, an uninterruptible power supply (UPS), 2000kV) is recommended in order to protect the instrument from unexpected electrical interruptions. If power is lost to the instrument, venting can be avoided using an automatic shutdown device; this monitors the AC power through an AC/DC converter connected to the same circuit as the UPS (but not the UPS itself) and triggers a timer to shut down the system if power is not restored in a certain (user configurable) amount of time.
- The correct configuration of “Acquility” software is necessary to ensure the valid operation of the instrument. All calibration values are automatically read into the software following calibration. However, these values can be verified or edited in the workspace editor.

### 3.2.2.2. *Determination of the composition of NR-PM<sub>1</sub>*

The COLOSSAL/ACTRIS SOP documents ([COST-COLOSSAL, 2021](#), and [COST-COLOSSAL/ACTRIS, 2022](#)) describe a standard method for determining the NR-PM<sub>1</sub> compounds and OA species concentrations in ambient air by using Q-ACSM and ToF-ACSM, respectively. We refer the reader to the [original standards](#). Below we summarise the most important topics.

#### *Method of operation for determining NR-PM<sub>1</sub>*

ACSM functioning is based on the differential collection of ionised molecular fragments, which can be differentiated upon on their mass.

The process starts with an isokinetic sampling of the particles. Then the aerosol enters the inlet (with a determined diameter cut-off cyclone) at a given flow and goes through a critical orifice and aerodynamic lenses which limits the upper size of particles and focuses the particle beam. Then, the

aerosol enters the vaporiser chamber, under high-vacuum conditions, particles are flash vaporised, and molecular fragments are subsequently ionised by electron impact (70eV) to be conducted to the detector. The detector can be either a quadrupole or time-of-flight detectors for Q-ACSM and ToF-ACSM, respectively. The quadrupole can quantify the concentrations of fragments per each mass-to-charge ratio ( $m/z$ ) ranging from 12 Th to around 120 Th for Q-ACSM and up to 250 Th for ToF-ACSM. The detector counts are transformed from intensity to mass concentrations through several conversive operations and parameters out coming from calibration procedures. Thus, the ACSM provides the time series of each of the  $m/z$  channels. A fragmentation chart quantifies the fragmentation of the NR-PM<sub>1</sub> constituents into the different  $m/z$  ratios according to lab experiments. Using deconvolution procedures, NR-PM<sub>1</sub> constituents' concentrations are obtained.

In order to eliminate the signals coming from the gas phase which would interfere with the PM composition determination, the instrument uses a switching valve mechanism for alternating filtered and non-filtered air measurements. In this way, the particle mass concentration and composition can be obtained by subtracting the filtered air (only gaseous compounds) concentrations from the ambient (particle-laden air) concentrations.

With these processes, the ACSM provides the time series of concentrations of the NR-PM<sub>1</sub> compounds. However, the time evolution of  $m/z$ -speciated organic aerosol concentrations and the uncertainty of each measurement are also stored in matrix form for posterior organic aerosol source apportionment applications.

### *ACSM performance criteria and test procedures*

In Table 3.2.1, the periodicity of the checks and the actions to be taken when the requirements are not met are shown. Respecting these checks and maintenance operations enables optimisation of the operating rate and maximises the quality of available data.

**Table 3.2.1.** Summary of checks and maintenance operations for Q-ACSM and ToF-ACSM (COST-COLOSSAL/ACTRIS, 2022).

Check and/or maintenance points	Frequency	Requirement	Corrective action
Acquisition software response	Daily	Scanning bar should be moving and Igor plots updated	Reboot Prisma, PC, software in this order.
Aerodynamic lens pressure in DAQ	Daily	Open valve pressures must be $1.3 \pm 15\%$ Torr and 1.6- 2.0 mbar (Q-ACSM, ToF-ACSM respectively) for $PM_{10}$ lenses, and $3.3 \pm 15\%$ Torr, 4 - 4.8 mbar (Q-ACSM and ToF-ACSM, respectively) for $PM_{2.5}$ lenses	Clean critical orifice. Verify pumps are working properly.
Vaporiser voltage	Daily	Initial setpoint	There is a recommendation to set the vaporiser temperature to 550 °C for capture vaporise. If the reading is off the 600°C, the vaporiser voltage can be slightly modified to meet this temperature so that the fragmentation process is not altered. However, a significant variation in the vaporiser temperature typically indicates that the thermocouple might have moved and its reading drifted, hence it is advised to stick to the detector shipping voltage.
Air beam	Daily	Stable at $10^{-7}$ ( $\pm 15\%$ ) amps for Q-ACSM and at is $1-5 \times 10^5$ ions/s for ToF-ACSM	Check SEM voltage is on. Tune SEM voltage if the air beam is significantly off $10^{-7}$ Amps (see sections 4.2.3, 4.2.4 in the COLOSSAL SOP document).
SEM voltage	Daily	Activated (ON)	Turn on and tune (Section 4.2.4 in the COLOSSAL SOP document)
Filament emission	Daily	1 mA $\pm$ 5%	Turn on the filament or change if broken.
Concentrations $NR-PM_{10}$ species	Daily	Mainly positive ( $> \pm$ detection limits)	If zero concentrations check valve, filament, voltages, filter turning, acquisition. If systematically negative check if particle filter valve is inverted or stuck in a position (see section 4.2.5 in COLOSSAL SOP document)
Turbo and MD1 pumps	Daily	Correct power and temperature	Investigation (leaks, fan functioning, damage on diaphragms...)
Dryer	Daily	20-60 %	Verification of the flow rate, integrity of the Nafion® membrane and pump.
MD1 backing pressure	3-6 months	$\pm 10\%$ of last check	Change diaphragm or pump

**Table 3.2.1. Continuation.**

Check and/or maintenance points	Frequency	Requirement	Corrective action
<i>Flow rate of the sampling system</i>	Each visit	Stable and equal to $(3 \pm 0.3)$ L min <sup>-1</sup> (PM <sub>1</sub> ) and to $(2 \pm 0.3)$ L min <sup>-1</sup> (PM <sub>2.5</sub> ).	Verification of the pump and sample line integrity.
<i>Flow calibration</i>	6 months	Check $(3 \pm 0.3)$ L min <sup>-1</sup> (PM <sub>1</sub> ) and $(2 \pm 0.3)$ L min <sup>-1</sup> (PM <sub>2.5</sub> ) using an independent flow metre.	Investigate leaks, pump performance.
<i>Instrument blank/leak check</i>	6 months or when changes in sample lines	Install HEPA filter on instrument inlet. Concentrations must be close to the instrument's detection limits (<±0.5 µg/m <sup>3</sup> ).	Concentrations must be close to the instrument's detection limits (leak, Nafion®, vacuum problem, clogged filter, etc.)
<i>Reset PrismaPlus baseline</i>	6 months or after SEM replacement	Reset baseline to avoid negative error matrix	Run amplifier offsets routinely (see section 4.2.9 in the COLOSSAL SOP document).
<i>Cleaning of the critical orifice</i>	6 months or when clogged	If flow rate drops 5% from the starting value.	
<i>m/z calibration</i>	6 months, before RIE calibration or after filament change	Check Prisma resolution and mass-to-charge (m/z) calibration	Check m/z 28 and m/z 128 (see section 4.2.10 in COLOSSAL SOP document).
<i>Heater bias voltage</i>	6 months, when RIE calibration or filament change	If checking - within 1V of previous value. Post filament change - tune.	Post filament change check daily for 1 week and return once stable.
<i>Cleaning the cyclone</i>	6 months or more often in dirtier location	Cleaning similar to another automatic PM measuring systems with DI water and detergent if required.	
<i>Cleaning the sampling line (from head to the lens)</i>	1 year	With compressed air and, if needed, with ultrasonic in a water-alcohol bath.	
<i>Cleaning of fans</i>	1 year	These include electronics box, pump1, under Prisma, internal to prism as and detector's fans (Q-ACSM) and of TPS panel fans (ToF-ACSM).	
<i>Replacement of the particle filter</i>	1 year	Preventive replacement, pressure difference should be less and 0.01 Torr between open and closed	
<i>Replacement of the three-way valve</i>	2 years	Preventive replacement	
<i>Change turbo pump lubricant reservoir</i>	4 years	<a href="https://support.aerodyne.com/knowledgebase/articles/KA-01144/en-us">https://support.aerodyne.com/knowledgebase/articles/KA-01144/en-us</a>	

## ACSM calibration

### Relative Ionisation efficiency calibration

The Response Factor (RF) (Ionisation Efficiency IE for ToF-ACSM) of  $\text{NO}_3^-$ , and Relative Ionisation Efficiencies (RIE) of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  are determined from measurement of 300 nm diameter particles of  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , respectively. The determination of RIEs for chloride and MSA may be necessary in some environments (see sections 5.5 and 5.6). Here, a summary of the procedure is presented, and the reader should refer to the [mentioned documentation](#) for more detailed explanations.

First, particles are generated from nebulising solutions of  $\text{NH}_4\text{NO}_3$  or  $(\text{NH}_4)_2\text{SO}_4$ . Particles are dried before size-selection achieving a relative humidity between 20 and 40% and then an aerosol diluter allows the user to dynamically change the aerosol concentration to provide a concentration range during calibration. Only 300 nm particles are size-selected using a Differential Mobility Analyser (DMA). Then an aerosol diluter allows the user to dynamically change the aerosol concentration to provide a concentration range during calibration. The use of a mixing tube downstream of the aerosol diluter is necessary to ensure the aerosols and diluting air are fully mixed before they reach the ACSM and CPC inlet. The outlet of the generation setup can be connected to the ½ inch sampling tube located downstream of the dryer to mimic the sampling setup. A CPC is used to measure the number concentration of 300 nm particles. [It should be connected to the ACSM sampling pump connector](#). The length of the tube should be minimised to avoid particle loss.

The calibration is proceeded in a point-by-point manner, by generating a known number of particles (measured from the CPC) and associating their calculated mass with the intensity signal detected by the ACSM. It is recommended that each calibration curve includes at least 7 data points, equally distributed over the expected concentration range in the investigated ambient air and starting from zero. After the whole dynamic range exploration, the RF or IE is determined by the signal of ions from  $\text{NO}_3^-$  species (30 and 46 m/z) from ammonium nitrate particles. From this value, the calibration slope intensity signal vs. input mass is calculated and associated with the Relative Ion Efficiency factor for  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  for ammonium nitrate and ammonium sulphate calibrations, respectively). This method is not biased by particle bounce. Indeed, ratios of  $\text{NH}_4^+$  from nitrate and  $\text{NH}_4^+$  from sulphate are used to estimate the collection efficiency of sulphate during calibration. For the calibration with ammonium sulphate, one should start with small concentrations and increase

slowly due to partly slow evaporation of ammonium sulphate hysteresis effects that can influence the calibration if done otherwise.

The obtained RF, and RIE values are to be entered in the data treatment software to apply these parameters to the final mass concentration determination. Also, other parameters recorded during the RIE calibration are stored and will be useful for posterior calculations (reference inlet pressure, reference flow, reference N<sub>2</sub> signal, reference temperature, etc.).

### m/z calibration (Q-ACSM)

For the Q-ACSM, the mass-to-charge (m/z) calibration of the quadrupole is based on water, air and naphthalene peaks. The naphthalene fragment ions, with a parent peak at m/z 128, come from an internal standard that is used to correct for ion transmission loss at high m/z in the quadrupole, as well as to calibrate the m/z scale.

In practice, this is a two-point calibration procedure using peaks at m/z 28 (N<sub>2</sub><sup>+</sup>) and naphthalene peaks at m/z 128 to “electronically” calibrate the analyser over the 10-150 *amu* range. These fragments provide in-situ measurements of ion transmission and thus can impact the RIT correction.

Nominal masses at m/z 28 and 128 can be compared to centred values obtained by fitting the signal as gaussians. If the *amu* difference is higher than +/-0.05 (threshold for acceptability for variance from m/z calibration perfectly set), m/z offset and slope adjustments have to be tuned until the N<sub>2</sub><sup>+</sup> and naphthalene peaks are centred at their nominal mass values (default set is 1.000 for the slope and 0.00 for the offset). Both are quite sensitive and need to be adjusted with caution in steps of 0.001.

Even if the m/z calibration is not supposed to change over time, it is important to check *amu* calibration once per half-year and after each maintenance into the vacuum chamber. The naphthalene signal varies from one instrument to the other, but the signal needs to be sufficiently intense to be detected on each MS to reduce measurement uncertainties when ion transmission is corrected.

### Corrections

#### RIT correction

The relative ion transmission correction (RIT) is applied in data processing by fitting the decay of several naphthalene ions and air signals through the spectra. The detector sensitivity to these signals

has been previously adjusted in the  $m/z$  calibration. The obtained decay fitting parameters are then passed to the software to adjust each  $m/z$  detector sensitivity to the actual measurements.

#### Air beam correction

The air beam is the measured signal in amperes (A) of  $m/z$  28 in the mass spectrum while the switching valve is in filter position. This is predominantly from  $N_2^+$  from atmospheric  $N_2$ . This value is taken as a reference to correct for variations in the ACSM's flow rate as well as changes in the instrument sensitivity, typically due to a decrease in the detector efficiency.

The air beam reference value for the Q-ACSM is  $10^{-7}$  A and  $10^5$  ions/s for the ToF-ACSM. This value is controlled by adjusting the secondary electron multiplier (SEM) voltage of the Prisma detector and following the tuning procedure described in the user's manual for Q-ACSM and increasing the detector voltage for ToF-ACSM. This tuning/voltage increase must be done before calibration and when the value has decreased by more than 15 % from the reference value.

During data processing, the concentrations measured by the ACSM are corrected, linearly, from the air beam variations around its reference value. If the air beam deviates more than 30% from its reference value, correction may no longer be valid, and the data should be investigated to ensure consistent response. A low value from the air beam can also be due to a closed inlet valve, a blocked critical orifice, or the SEM detector or filament's power being off.

#### Collection efficiency correction

An important parameter to be considered is the collection efficiency (CE), which translates how efficiently the sampled particles go through the inlet, lens, vacuum chamber and are impacted onto the vaporiser. For online ACSM data acquisition and for instruments equipped with a standard vaporiser, a default collection efficiency of 0.5 (CE=0.5) is commonly set on the instrument software. For ACSM equipped with the so-called capture vaporiser, a constant CE value of 1 should be used since the special geometry of the vaporiser prevents this particle loss. This collection efficiency should be adjusted post hoc to consider its variation over time, notably depending on the chemical composition of the sampled aerosols.

Middlebrook et al. (2012) proposed a procedure to accurately estimate CE under various conditions. For standard vaporisers, time-dependent CE values mainly fluctuate with the ammonium nitrate mass fraction (ANMF), aerosol's acidity, and relative humidity.

Contrarily to the aforementioned corrections, CE-related variations are not accounted for by the acquisition software. A CE calculation software can be used for time-dependent CE calculation to be posteriorly used to correct the NR-PM<sub>1</sub> concentrations and organic matrix data.

#### Determination of detection limits

It is necessary to determine detection limits (DL). The obtained values represent the thresholds under which the instrument noise would be as high as the actual measurement, so they are used for error calculation, data validation, etc. The ACSMs ordered from lower to higher DL are: ToF-ACSM-X, ToF-ACSM and Q-ACSM.

The procedure for determining DLs consists in placing a HEPA filter on the sample inlet and measuring in “acquisition” mode for at least 3 hours.

#### Measurement procedure

The [aforementioned documents](#) provide thorough recommendations for measurement planning, installation, and initial checks on site. For further advice on maintenance of the instrument, one can consult the Aerodyne ACSM Maintenance knowledge base (Aerodyne, 2024), available upon sign in.

#### Other instrumental recommendations

In order to validate the measure data, the reader should address the steps in sections 6.1 and 6.2 in [COST-COLOSSAL 2021 and COST-COLOSSAL/ACTRIS 2022](#) for Q-ACSM and ToF-ACSM, respectively, and verify the correct status of the instrument during measurement according to the values established in Table 3.2.1 of the above sections. This includes the calculation of the DL of each species (procedure detailed in “corrections”) and the evaluation of the measurements upon these thresholds.

Also, it is advisable to check the inter comparability of ACSM outcomes with independent measurements out coming from co-located instrumentation. Recommended instrumentation for such intercomparisons can be found in the ECAC website as well, in “Guidelines for comparison of ACSM measurements with co-located external data”, cited from now on in this document as [COST-COLOSSAL \(2019\)](#). This practice allows to validate ACSM outcomes by comparing them with trustworthy reference measurements, and includes two main steps, summarised below.

- Mass closure checks: It is possible to “reconstruct” PM mass concentrations as the sum of major chemical species, including NR species measured by the ACSM. To do so, it is highly recommended to also account for refractory material, such as equivalent black carbon (eBC) or

elemental carbon EC), obtained from optical and/or thermo-optical instrumentation. The use of aethalometer data is not that straightforward. The BC data in  $\mu\text{g}/\text{m}^3$  produced by optical instruments can be far away from actual mass concentrations. This is why “eBC” is used. To get mass concentrations from light absorption measurements, specific MAC values shall be determined by from regressions between absorption and EC measurements (in the same size fraction). The reader is addressed to [RI-URBANS’ ST2 on Black Carbon](#). Therefore, in the most common case of submicron measurements and using an absorption photometer, the following equation should be applied:  $\text{PM}_{1, \text{chem}} = \text{NO}_3^- + \text{SO}_4^{2-} + \text{NH}_4^+ + \text{Cl}^- + \text{OA} + \text{eBC}$ . The sum of the PM1 constituents is to be compared with independently determined PM1 concentrations measured by gravimetric offline analyses, Tapered Element Oscillating Microbalance equipped with Filter Dynamic Measurement System (TEOM-FDMS), or estimated from the data obtained using Mobility Particle Size Spectrometers (MPSS), optical devices, , . When PM mass concentration measurements are not available for the aerosol size fraction used by ACSM measurements, different size fractions can be compared, keeping in mind that this difference can substantially influence the regression correlation coefficient, slope and intercept.

- Individual chemical species. it is preferable to compare ACSM chemical species concentration to corresponding dataset obtained from online measurements (from AMS, other ACSMs, ion chromatography downstream of Particle-Into-Liquid Sampler (PILS), Steam Jet Aerosol Collector (SJAC) systems, Total Carbon analysers (TCA), etc.), rather than with off-line filter-based chemical speciation to limit the risk of sampling artefact influence. If online chemical composition concentrations are not available, then comparisons with offline filter based can be performed, focusing on species which are little prone to sampling artefacts (e.g. sulphate).

It is recommended to perform these comparisons both by compiling time series in a single graph and using scatterplots. The first charts may help to easily and precisely identify when outliers or suspicious periods occur. The second ones enable an easier analysis of the correlation and/or deviations between the compared datasets. It is highly recommended to use orthogonal regressions, as, generally, none of the compared datasets may be considered to be without error.

### 3.2.3. Measurement of trace elements and metals

Airborne particulate matter includes metals (e.g., Ca, Fe, Pb), non-metals (e.g., S, Cl), and metalloids (e.g., Si, As). By definition, a metal is a chemical element being a good conductor of both electricity and heat and readily loses electrons to form cations and ionic bonds with non-metals. These also

have high melting and boiling points and are found solid at ambient temperature. In opposite, non-metals are poor conductors of heat and electricity, and generally have low melting and boiling points. Metalloids, often called semiconductors, have intermediate electrical conductivity between metals and non-metals. PM elements are persistent species that can be found at low-level (trace) concentrations in the atmosphere. Their measurement is important due to their potential adverse impacts on human health and the environment, and their potential use as source tracers.

As aforementioned, there are three commercially available instruments that provides capabilities in real-time analysis of trace element and metal samples: the Xact 625i (Cooper Environmental), the Atmospheric Heavy Metals On-line Analyzer EHM-X100 (Skyray Instrument Ltd., China) and the Particulate Monitor with X-ray Fluorescence PX-375 (Horiba Ltd., Japan). The Xact 625i instrument is currently the only instrument used regularly within Europe and due to available knowledge and experience the following guides will focus on this instrument. The Xact 625i simultaneously measures up to 67 elements with an atomic number between aluminium (Al) and uranium (U). The measurement is based on reel-to-reel filter tape sampling followed by non-destructive X-ray fluorescence (XRF) analysis of elements in the resulting particulate matter deposit. The automated system is engineered to provide users with continuous, near-real-time metal and trace element concentrations.

The current document does not provide specific standards or recommendations like for the other advanced AQ measurements. Detailed information about the operation of the instrument is available at <https://cooperenvironmental.freshdesk.com> or provided by the manufacturer Cooper Environmental. Instrument description can also be found in Furger et al. (2017), Furger et al. (2020), Manousakas et al. (2022), Tremper et al. (2018) and the references therein.

### *3.2.3.1. Sampling and conditioning*

#### *Sampling*

As an example, Xact 625i draws ambient air at  $16.7 \text{ L}\cdot\text{min}^{-1}$  flow rate through a PM size-selective inlet and a sampling line of 31.75 mm (1.25") diameter (standard line used by the manufacturer) with an external diaphragm pump. The inlet should be installed at least 1 m above its supporting structure and 2 to 15 m off the ground with a minimum of 2 m of unobstructed air flow in all horizontal directions, according to the U.S. EPA guidelines 2.12 (U.S. Environmental Protection Agency, 2016). The sampling line should not exceed 5 m in length, and supporting braces should be installed on the shelter roof if there is potential for swaying from high wind conditions. The Xact is

compatible with various inlets including low volume total suspended particulate (TSP), PM10, PM2.5, and PM1. It can also be equipped with an automated inlet switching system allowing for the alternating collection of samples from two different sizes (e.g. PM2.5 and PM10). In the case of PM2.5/PM10 association, the approach consists in a split system with a direct line between the PM10 head and the Xact, and a bypass line separating from the direct line after the PM10 head, containing the PM2.5 cyclone (Furger et al., 2020; Manousakas et al., 2022). Another system is also currently in use, with PM10 and PM2.5 heads and only one switching valve between them, the PM10 line is straight while the PM2.5 line comes in next to it. The switching is steered by two motorized ball valves, which are controlled by a voltage signal provided by the Xact. The ambient air is then drawn across a reel-to-reel Teflon filter tape to collect particles. After each sampling interval, the tape is moved in the analysis area.

The instrument set up also incorporates external meteorological sensor (temperature, pressure, relative humidity, wind direction and velocity) which should be installed at least 1 m above the shelter, Xact sampling inlet or any other obstructions (such as trees or buildings). Ambient temperature and pressure readings are used along with a mass flow control to maintain the constant volumetric sampling rate of 16.7 L min<sup>-1</sup> needed to have the size cuts correct.

### *Drying*

The sampling line is generally equipped with an inlet tube heater for heating to 45 °C above the dew point before sampling through the filter to avoid water depositing on the tape. This heating is not problematic due to the low volatility of the measured elements.

### *Particle losses*

Similarly, to ACSM instrumentation, the particle losses in the sampling system can be evaluated using the PLC tool in Igor Pro software (<http://www.mpch-mainz.mpg.de/~drewnick/PLC/>). However, the use of the EPA standard sampling system described above should prevent any losses, or getting less than 2% of the particle mass lost in the particular case of the switching system (Furger et al., 2020).

### *Sampling frequency*

Xact 625i performs continuous measurements for the user-selected sampling time (between 15 and 240 minutes), which shall be such that the amounts of analytes collected are above the detection limits for the elements of interest. The reel-to-reel filter tape allows the Xact to perform sampling

and analysis continuously and simultaneously, except for tape advancement (~20 seconds) and once daily automated QA checks (30 minutes).

### *Performance criteria and test procedures for the sampling and conditioning system*

Some standard requirements for an effective Xact deployment must be met and are listed as following:

- The Xact needs to be installed in a protected air-conditioned environment with thermo-regulated conditions (around  $20 \pm 3^{\circ}\text{C}$ ). Any fast variation of temperature could badly affect the results.
- The Xact operates on 110-230 VAC, 50-60 Hz, 10 A.
- The Xact Control Program and the Automated Data Analysis and Plotting Toolset (ADAPT) software are provided and used for Xact acquisition. The tools are run under Windows environment and needs to be regularly updated.
- The instrument should be connected to the Internet to allow remote access control of the instrument to inspect the running acquisitions.
- An inverter (e.g. uninterruptible power supply (UPS)) is recommended in order to protect the instrument from unexpected electrical interruptions.
- Due to the presence of X-Ray-producing equipment, safety precautions must be strictly observed. Radiation permits are needed to run this instrument and users need to contact radiation safety departments to this end. The user must avoid energising the X-Ray tube, or even operate the Xact, if the safety features of the instrument have been damaged, defeated or the instrument is not operating correctly.

For the proper functioning of the sampling and conditioning system, a set of test procedures, performance and operational checks is needed. Note that **the detailed procedures are provided in the manual from the manufacturer** and will be detailed in the future SOP in development by ROXI and ACTRIS. A summary of the main key points is described below:

- **Filter tape replacement:** Used filter tape contains sample deposits that are collected every two inches on the tape. Xact instrument requires the user to manually install new filter tape rolls. Changing the filter tape takes approximately 15 minutes to complete and should occur according to the frequency of the sample times shown in the Table 3.2.2. If the filter tape breaks, Xact will automatically go into Stop mode and issue alarm on Xact Control home screen. The break in the filter tape can be repaired by attaching the broken ends together with adhesive tape.

**Table 3.2.2.** Occurrences for changing filter tape of the Xact according to the time resolution.

Sample Time in Minutes	Approximate Frequency of Tape Change
15	Once every 6 days
60	Once every 25 days
240	Once every 3 months

- **Leak check:** This test should occur after every reinstallation of the Xact or anytime a connection break occurs in the flow system. It can be performed by removing the PM inlet and installing a leak tester (Sample inlet ball valve) over the sampling line. By slowly closing the leak tester valve the pump can create vacuum across the Xact flow system. The sample pressure reading will fall below 130 mmHg (if not, the system may have a leak) and Xact software will shut down the pump. The results of the leak check are obtained after 90 seconds. Once finished, it is needed to open the leak tester valve very slowly to prevent sudden release of vacuum pressure and thus damage to Xact 625i flow sensor. If the leak rate is higher than 150 mmHg/min, the Xact failed the leak test, and the user must examine the sample tubing and vanes before repeating the process. If the instrument continues to fail the test persistently, it is necessary to contact the manufacturer or service representative for further investigation of the instrument state.
- **Flow check:** This test should be performed after reinstallation of the Xact and can be done right after a leak check. With the leak tester installed over the sampling line, a certified reference flow meter has to be connected to the sample inlet ball valve. Once the flowmeter is stabilised to the proper atmospheric temperature and barometric pressure (after ~60 sec), three flow rates (15.0, 16.7 and 18.4 L.min<sup>-1</sup>) have to be tested by adjusting the pump flow within the Xact software. The flow check should be considered as valid if the difference is less than 1% between the reference flowmeter values and Xact software flow rate readings, and temperature and pressure are within 10% of the reference values. If not, it is needed to perform a flow calibration.
- **Flow calibration:** The flow must be calibrated if the flow check fails, provided that the Xact has successfully passed the leak check. Calibration is performed using the same setup as the flow check. This procedure involves providing a reference flow rate value from the flowmeter to the Xact software, which then automatically calibrates the Xact's flow system.

- **Regular maintenance:** Sampling line, PM inlet and external meteorological sensors must be cleaned on an annual basis, like for every other analyser. Moreover, the diaphragm pump kit needs to be changed every year to insure a sufficient depression into the system.

### 3.2.3.2. *Determination of the particulate trace elements atmospheric concentrations*

#### *Determination of atmospheric concentrations*

The instrument determines element concentrations by measuring the volume of the air sampled during the sampling time and the mass of each element in the sample deposit collected during that time (see section 3.2.3.1., sampling). To determine the mass of each element in the deposit, the Xact uses the energy Dispersive-X-Ray fluorescence (ED-XRF) spectroscopy method.

Briefly, the atoms from the deposit are excited by an X-Ray beam produced by a Rhodium anode (50 kV, 50 Watt) and fluoresced photons are counted with a solid-state detector. The energy of the produced fluorescing X-Ray is characteristic of the element it was emitted from. This analysis is performed in three successive energy conditions, which target three different suites of elements. The fluorescing X-Ray spectra are analysed by the quantitation software package “XRS-FP program”. Here, the intensity of the characteristic radiation (sorted per energy) is directly proportional to the amount of mass of each element in the sample. Eventually, the instrument provides the time series of atmospheric concentrations of the particulate elements detected.

Daily automated quality assurance checks are performed every night at midnight. First, an energy alignment is performed (00:00-00:15), consisting of an energy calibration using a dynamic rod coated with Niobium (Nb) and Chromium (Cr) inserted into the analysis area to ensure that the spectral peaks for each element are at the correct energy levels. Then, an automated upscale measurement using Chromium (Cr), Lead (Pb) and Cadmium (Cd) is done immediately after the energy alignment (00:15-00:30) to monitor the stability of the instrument response.

It is noteworthy that lightest elements, such as Al (and Si), can be affected by noise and interference in the XRF analyses using Xact 625i. These elements emit X-rays of low energy subject to scattering and absorption, and their signal may be more impacted by secondary fluorescence from heavier elements or the interactions with the complex air matrix. Therefore, these data should be considered with caution.

The performance of Xact 625i was evaluated against the PX-375 instrument in a recent study conducted at the regional background site of Kosetice, Czech Republic (Windell et al., to be

submitted). The measurements of both instruments were compared to reference filter-based ICP-MS analyses and proved their capabilities with average  $R^2$  values across elements of 0.89 and 0.79 for Xact 625i and PX-375, respectively. However, discrepancies in slopes were observed between the two instruments for elements with concentrations near their detection limits (Al, Si, As, Cu, Ni and Cd).

### *Xact performance criteria and test procedures*

Checks and maintenance operations for QA/QC should be performed to ensure the good performance of the Xact. The procedures and the related outputs are listed below:

- **QA upscale tracking:** The QA upscale data should be examined regularly for deviation from the reference values (set after each X-Ray tube calibration in the Xact Control Program) over time. Slow decline in QA Upscale value is expected over long period of Xact 625 usage (1-3 years) due to decrease in excitation from the X-Ray tube. If the QA Upscale metal concentrations continue to deviate by more than 10% from the reference values over time, a XRF Calibration Check need to be performed. If the Xact fails the check, it is recommended to contact the manufacturer or service representative. In the case where there is a deviation of these values after reinstalling a new X-Ray tube, it can be an issue with the dynamic rod positioning, which need to be adjusted then.
- **QA blank check:** The check consists of analysing clean spots on the filter tape at the three energy conditions. The procedure must be done in the Xact Control Program and with a clean tape installed (with enough distance from the last sampling spot). Routinely monitoring the blanks enables to capture any deviations over time due to potential contamination.
- **XRF calibration check:** This procedure evaluates the performance of the XRF system by examining spectra for the set of element standards provided with Xact. The number and type of element standards used for this check are specific to custom-calibrated Xact. Element standards are pure element standards and are free from any interfering elements. These standards contain a known amount of each element on a nucleopore substrate that is mounted on standard holder provided by the manufacturer. The check should be performed with five recommended standards (all analytes and not interfering elements), two for each energy conditions 1 and 2 (EC1 and EC2) and one for energy condition 3 (EC3). The standards should be manipulated with nitrile gloves, and their analysis based on the Xact calibration guide, providing the energy condition and acquisition time to be used for each element standard. The procedure is further detailed in the manual from Cooper Environmental. The calibration check is successful if the difference between the mass of

the standard element measured with the Xact and the mass reported in the guide is within  $\pm 10\%$ . A failure in the calibration check could be related to several reasons (such as degraded or contaminated standards, or wrong positioning in the holder), and will necessitate some support from the manufacturer or service representative.

Note that QA blank and XRF calibration checks are recommended every 3-6 months.

The Xact Control program provides also automated warning status alarms for helping the users with troubleshooting. The complete list of available alarms is given in manual from the manufacturer.

### *Xact recalibration*

Since a new X-ray tube begins to deteriorate and lose excitation potential immediately after its construction, estimated lifespan can be limited to 1 to 3.5 years maximum according to manufacturer and users experience. After this estimated period, the tube breaks and needs to be replaced. Until now, there is no existing method to monitor the X-ray tube lifespan and performance. Tracking either the filament current or the Nb internal standard values could be possible indications and need to be investigated. It is also recommended to adjust the current of EC1 to increase the lifespan of the X-ray tube and reduce costs. However, this procedure should only be applied in locations where the EC1 elements are abundant as it will lead to higher detection limits (DLs).

Xact recalibration is performed when a new X-Ray tube is installed or if the user wants to monitor a group of elements different from those the instrument was calibrated for at the factory. Since the Xact is a precisely calibrated instrument for user requested elements of interest, the entire instrument must be recalibrated.

The Xact recalibration is described as follows: the newly installed tube needs first to be warmed-up and the Nb rod has to be removed for the full procedure. Tape blanks and all element standards (from the custom list) must be run, following the QA blank check and XRF calibration check procedures, respectively. Cooper Environmental's personnel must perform the recalibration using the spectra generated during the two previous procedures. Once done, the Nb rod needs to be reinstalled, and the position readjusted. Note that the Nb internal standard level will change and need to be adjusted. A new average Nb reference value should be calculated by averaging data for 5 hours of measurements.

It should be emphasised that element standards may deteriorate over time, potentially leading to inaccurate calibration of the targeted elements. It is important to regularly control the state of the standards and replace them if necessary to ensure reliable calibration. The use of these single-element standards without a real complex matrix may also introduce uncertainties into the calibration of elements.

### *Corrections*

One of the advantages of Xact instruments is the automation of element concentration calculations, which does not need any post-correction. The software automatically applies X-Ray spectra deconvolution using multiple reference spectra stored in an electronic library, fitting the unknown spectrum using a least-squares fitting method. Final concentrations and uncertainties are reported in near real-time for each sampling time.

Users can integrate additional elements into the custom-calibrated Xact's list. By following the recalibration procedure (see section on Xact recalibration) only to these specific elements, new spectra can be added to the reference ones. Subsequently, Cooper Environmental personnel can recalculate the concentrations of these elements in post-processing from the last X-Ray tube installation.

### *Measurement procedure*

Furger et al. (2017), Furger et al. (2020), Manousakas et al. (2022), Tremper et al. (2018) provide thorough recommendations for measurement planning, installation, initial checks and maintenance on site. For further instruction guides and information on the Xact, one can refer to the documentation with all procedures from Cooper Environmental using the following freshdesk SCI service link: <https://cooperenvironmental.freshdesk.com/support/login> (available upon sign in).

### *Quality control, quality assurance and measurement uncertainty*

Running Xact instruments following the best practices previously outlined will ensure to successfully generate good quality measurement data. However, several recommendations can be implemented to control and ensure the validity of Xact data during post-treatment:

- It is necessary to compare low concentration data with the detection limits (DLs) of each element, corresponding to the minimum threshold for which the concentrations do not exceed the background signal of the instrument. These values are provided by the manufacturer and are described as follows:

$$\sigma_0 = \frac{\sqrt{R \times t \times I}}{S \times t \times I}$$

Where  $\sigma_0$  is the 68% confidence level detection limit,  $R$  is the background count rate,  $t$  is the live time of the element,  $I$  is the current and  $S$  is the sensitivity. Then,

$$DL_{\sigma_0} = A \times \frac{\sigma_0}{V}$$

With  $A$  the sample deposit area and  $V$  the air volume collected during the sampling time.

For measured data either below the DLs or equal to 0 (Manousakas et al., 2022), it is suggested to replace the value with  $DL/2$  (Polissar et al., 1998). Users are also advised to calculate their own detection limits for each element by conducting field blanks. To do this, a HEPA filter has to be installed on the sample inlet while running the Xact for a minimum of 12 hours. The measurements are used to calculate the DLs, corresponding to three times the standard deviation of the measured concentrations (Poisson statistics). It may be useful to perform field blanks twice a year for QA/QC purposes.

Note that the analytical uncertainty for each element and time points is calculated by the Xact software and includes all the following uncertainties:

$$u_T = A_c \times \sqrt{u_{dm}^2 + u_f^2 + u_v^2 + u_a^2 + u_{sm}^2}$$

With  $u_T$  the total analyte measurement uncertainty,  $A_c$  the measured analyte concentration,  $u_{dm}$  the deconvolution mass uncertainty,  $u_f$  the flow sensor uncertainty,  $u_v$  the volume summation uncertainty,  $u_a$  the sample deposit area uncertainty and  $u_{sm}$  the calibration uncertainty of the pure element standard.

- Individual element Xact measurements can be compared to the corresponding measurements obtained using other methods. As recommended by Furger et al. (2017) and Tremper et al. (2018), comparisons can be carried out using filter samples (e.g., quartz or mixed cellulose ester filters) collected with a particle sampler. These filters can be analysed by ICP-MS or ICP-OES to compare a wide range of metals. Other offline analyses, such as ion chromatography, can be performed for Ca, Cl, K, or S, assuming that these elements occur mainly as water soluble species (e.g. sulphate for S). However, the impact of the heating at 45°C should be evaluated when analysing contents of specific ions. Then this subset of components can also be determined with online ion

chromatography approaches, such as the PILS or MARGA ambient ion monitor. Additionally, S and Cl measured with Xact can be compared with high-time resolution  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  data from ACSM or AMS, keeping in mind that a different size fraction addressed by these instruments can substantially influence the comparison. Comparisons between Xact and these techniques should show good agreement, with significant  $R^2$  values ( $>0.7$ ) and slopes close to 1 ( $\pm 15\%$ ). Note that the mentioned thresholds may be reviewed in any further SOPs to agree with the ROXI community.

Xact data time series can be affected by several outliers or suspicious peaks. These data points are considered as electronic spikes, local contamination, or erroneous high concentrations arising due to errors between the control and deconvolution of spectra, and those should be invalidated. To facilitate the detection of outliers, it is suggested to apply statistical techniques such as median/mean absolute deviation estimation, mean plus three standard deviations method or the upper whisker boundary of a box plot. Outlier detection should also rely on the user's knowledge of his own dataset. Monitoring the deviation of the Nb value from the reference one (see section on Xact recalibration) is also relevant for QA/QC purposes and potential data invalidation.

### 3.3. Data Management

The EBAS database, a major archive for data on atmospheric constituents worldwide, is hosting data of different research programs and infrastructures such as European Monitoring and Evaluation Programme (EMEP) or the WMO-GAW programme, among others. The EBAS database aims to document quality assured data, secure its long-term storage, and provide users for access to atmospheric composition data generated by international and national frameworks and research projects. Templates and tools for submitting data to EBAS of the different atmospheric variables and parameters are available at <https://ebas-data.nilu.no/>.

For official AQ measurements in Europe the European Environmental Agency's database is expected to collect the data produced by supersites associated to the NAQD.

#### *Offline speciation*

The templates for submitting offline chemical speciation data are:

<https://ebas-submit.nilu.no/templates/EC-OC/all>

<https://ebas-submit.nilu.no/templates/Inorganic-air-aerosol-chemistry-filter-based/lev2>

<https://ebas-submit.nilu.no/templates/Heavy-metals-in-aerosol-particle-phase/lev2>

## *ACSM*

The EBAS database is the recipient for ACSM data produced by ACTRIS platforms. AQMNs generally use their own Data Management Plans, fitting internal/national requirements and software packages used historically.

A comprehensive data submission tool has been developed called ACMCC\_Export (Jean-Eudes Petit, at CEA/LSCE), suitable both for Q-ACSM and ToF-ACSM. This software also includes a flagging panel which allows to filter data upon certain metadata criterions. ACMCC provides training for the use of this tool through data upload workshops imparted at their facilities. Also, a near-real time EBAS data submission tool is under implementation at several sites in Europe.

## *Elemental composition*

Online XRF instruments are relatively new and even though it is increasingly used across Europe. EBAS is collecting data already on PM speciation, and these protocols of data submission and format should be followed. A local protocol has been designed for submitting data to Defra (Department for Environment, Food & Rural Affairs) database in United Kingdom. It is worth noting that the recent integration of ROXI user group to the ACTRIS network might initiate the future development of an export tool for releasing particulate elemental concentrations and uncertainties in the EBAS requested format.

## 4. PAN-EUROPEAN OVERVIEW OF PM SPECIATION ACROSS URBAN ENVIRONMENTS

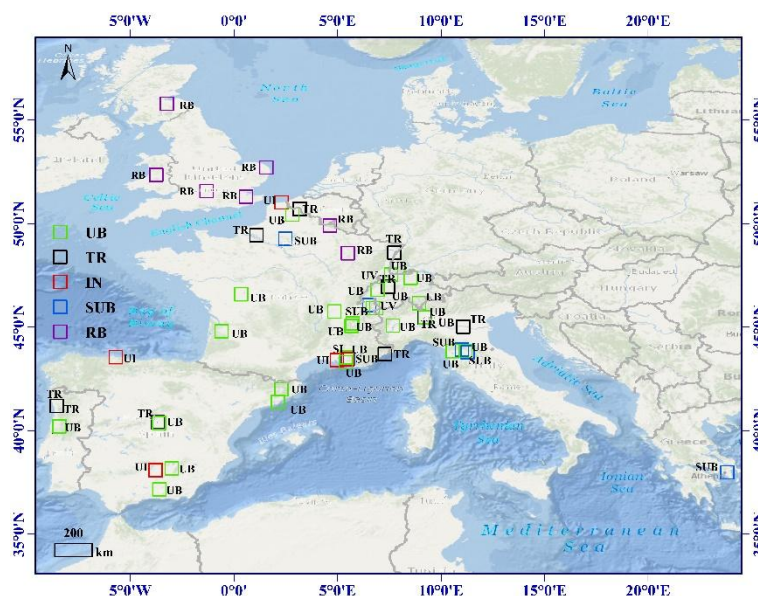
### 4.1. Offline PM speciation

#### 4.1.1. Trace elements

RI-URBANS compiled datasets of trace elements from 55 sites provided by AQMNs, research projects, and research supersites (Liu et al., 2024). The dataset spans a decade, covering the years 2013 to 2022, with series of data for each site covering a minimum of one year. The data come essentially from 7 countries: France (24 sites), Italy (9), Spain (8), Switzerland (5), UK (5), Portugal (3), and Greece (1) (Figure 4.1.1). The overall data base represents 16864 daily samples. These include (Figure 4.1.1):

- Twenty-six urban background (UB) sites covering most of western Europe: Basel (BAS\_UB), Barcelona (BCN\_UB), Florence Capannori (CA\_UB), Florence Calenzano (CAL\_UB), Coimbra (COIM\_UB), Granada (GRA\_UB), Grenoble CB (GRE-cb\_UB), Grenoble FR (GRE-fr\_UB), Grenoble VIF (GRE-vif\_UB), Lens (LEN\_UB), Lyon (LYN\_UB), Madrid E. Vallecas (MAD-EV\_UB), Magadino (MAG\_UB), Manlleu (MAN\_UB), Milano (MIL-air\_UB), Milan Pascal (MIL-pas\_UB), Marseille Longchamp (MRS-LCP\_UB), Aix-en-Provence (MRS-AIX\_UB), Payerne (PAY\_UB), Poitiers (POI\_UB), Talence (TAL\_UB), Turin (TUR\_UB), Villanueva Arz (VIL\_UB), Zurich (ZUR\_UB), Chamonix (CHAM\_UV, with UV referring to UB sites in intra-mountainous valleys), and Passy (PAS\_UV).
- Ten traffic (TR) sites: Bern (BER\_TR), Coimbra (COIM\_TR), Madrid Esc. Aguirre (MAD-EA\_TR), Milan Senato (MIL-sen\_TR), Milan Schivenoglia (MIL-shi\_TR), Nice (NIC\_TR), Porto (PORT\_TR), Roubaix (RBX\_TR), Rouen (ROU\_TR), and Strasbourg (STG\_TR).
- Five industrial (IN) sites: Bailen (BAI\_UI, with UI referring to UB-IN environments), Dunkerke-Grande Synthe (DKI\_UI), Gijon/Aviles (GIJ\_UI), Port de Bouc (PdB\_UI), and Gardanne (GAR\_SI, with SI referring to sub-urban background industrial environments).
- Seven sub-urban (SUB) sites: Malet (MAL\_SUB), Meyreuil (MEY\_SUB), Nogent sur Oise (NGT\_SUB), Marnaz (MNZ\_SUB), Athens Demokritos (DEM\_SUB), Florence (FLO\_SUB), and Florence Montale (MON\_SUB).

- Seven rural background (RB) sites: Auchencorth Moss (ACTH\_RB), Harwell (HAR\_UB), Cwmystwyth (CWM\_RB), Detling (DET\_RB), Heigham Holmes (HAM\_RB), Andra OPE (OPE\_RB), Revin (REV\_RB).



**Figure 4.1.1.** Location of the sites supplying trace elements concentration data for the present overview and the type of station. UB/UV, urban background and urban valley; TR, traffic; SUB, sub-urban background; IN, industry (UI, UB-industry, SI, SUB-industry); RB, rural background. Adapted from Liu et al. (2024).

#### 4.1.1.1. Measurements of trace elements

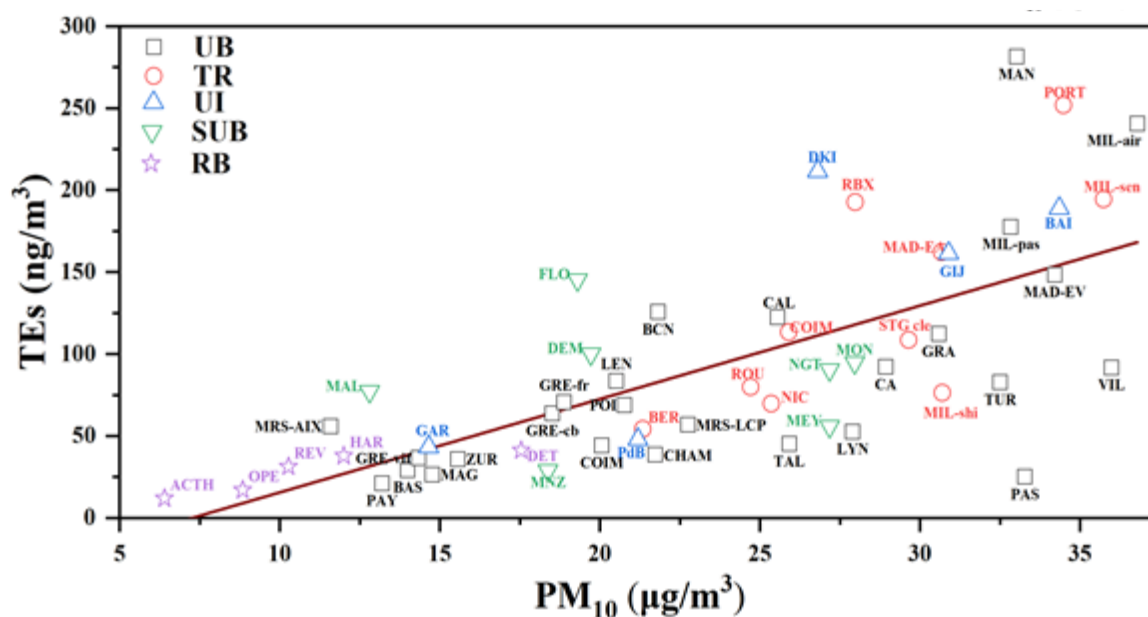
Measurements of trace elements were conducted at the different stations using a variety of approaches, including (i) Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 39/55 sites), (ii) Particle Induced X-Ray Emission technique (PIXE, 13/55), and (iii) X-Ray Fluorescence (XRF, 4/55). For ICP-MS analyses, PM samples have to be acid-digested using a combination of acids. While for the trace elements regulated in the EU AQ Directives, HF is not required for the sample digestion, for specific trace elements, such as Al and Ti, this acid is required to attain bulk dissolution (Querol et al., 2001). Furthermore, when analysing V, Ni and Cr, among others, in high dust-content PM samples, only a part of the bulk content of these elements is determined when using the digestion method described in European standard EN14902:2005, because the fraction of these occurring into aluminium silicate structures is not dissolved.

Twenty trace elements in PM<sub>10</sub> were selected for this overview, including As, Ba, Br, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Rb, Se, Sr, Ti, V, Y, Zn, and Zr. Among these, Cd, As, Cr, and Ni are classified as carcinogenic elements (WHO, 2007; Dimitriou and Kassomenos, 2017). It is worth mentioning that

Sn and Sb were not included because these elements were not determined in most sites where PIXE and XRF analyses were applied.

#### 4.1.1.2. Status of trace element data availability and concentrations in Europe

Figure 4.1.2 shows average total trace element concentration (sum of 20 elements) at each monitoring site during the monitoring period, emphasising obvious differences in trace element concentrations across the seven European countries. These are roughly correlated with PM10 concentrations (Figure 4.1.2), and average  $90 \pm 66 \text{ ng/m}^3$  across all monitoring stations.



**Figure 4.1.2.** Cross correlation of the average concentrations of 20 trace elements (sum and PM10 mass concentrations from the 55 European datasets compiled in this review. UB/UV, urban background and urban background in an intra-mountainous valley; TR, traffic; IN, industry (UI, UB-industry, SI, SUB-industry); SUB, suburban background; RB, rural background. Adapted from Liu et al. (2024).

Differences in trace element concentrations in PM10 were also noticeable in different regions and spaces. Specifically, concentrations decreased according to the site types as expected, with TR and IN ( $137 \pm 128$  and  $136 \pm 149 \text{ ng/m}^3$ ) > UB ( $112 \pm 117 \text{ ng/m}^3$ ) > SUB ( $81 \pm 74 \text{ ng/m}^3$ ) > RB ( $27 \pm 11 \text{ ng/m}^3$ ). These results suggested that industrial and road traffic pollution sources were the primary contributors to trace elements in PM10. Many studies report that in urban areas brake and tyre wear from vehicles is the main source of a number of trace elements, including Cu, Fe, Zn, Sn, Sb, Ba, among others (Amato et al., 2016, among others). Parviainen et al. (2019) studied trace element pollution in the highly industrialised city of Huelva, Spain, finding that trace element concentrations were extremely high within 1 km of industrial parks and gradually decreased beyond

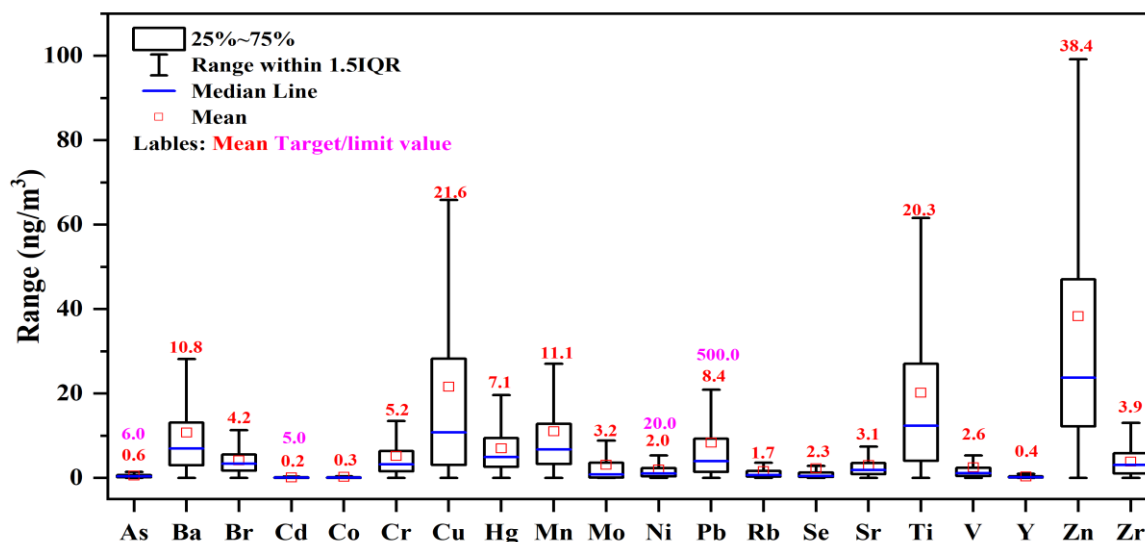
with distance. Similarly, Wang et al. (2013) found that atmospheric trace element concentrations were higher in industrial areas than in residential areas in Shanghai. Obviously, the industrial contribution to trace element concentrations depends on the type of industries (see Querol et al., 2007).

It is worth noting that the intramountainous valleys of CHAM\_UV and MNZ\_SUB exhibited relatively lower trace element concentrations, attributed to the absence of industrial and waste incinerator activities, and relatively low traffic density, in CHAM\_UV, where anthropogenic emissions mainly stem from road traffic, residential heating, and agricultural activities (Brulfert et al., 2006; Weber et al., 2019; Quimbayo-Duarte et al., 2021). Conversely, at MNZ\_SUB downstream of Passy, a ventilation zone forms due to a jet-like structure at the valley exit (Quimbayo-Duarte et al., 2021), significantly reducing trace elements and PM<sub>10</sub> levels, while emissions concentrated within this zone.

Data gathered from UB sites evidenced elevated levels of trace elements in Italy, Spain and Portugal, with average concentrations of the sum of the trace elements in PM<sub>10</sub> in the range of 155-165 ng/m<sup>3</sup>. Figure 4.1.2 indicates that five UB sites (PAS\_UB, VIL\_UB, TUR\_UB, LYN\_UB, and TAL\_UB), as well as specific TR, UI and SUB sites (MIL-shi\_TR, NIC\_TR, PdB\_UI, MEY\_SUB), record relatively high PM<sub>10</sub> concentrations but relatively low ones of trace elements. Conversely, in certain UB, TR and SUB sites (MAN\_UB, MIL-air\_UB, PORT\_TR, RBX\_TR, FLO\_SUB, and MAL\_SUB) the relatively lower concentrations of PM<sub>10</sub> coincided with relatively high ones of trace elements. Such results clearly indicate the role of various sources (like marine emissions or domestic biomass burning) in modulating the PM mass but not the trace element concentrations.

#### *4.1.1.3. Concentrations of individual trace elements*

AQ limit/target values for trace elements in European AQ Directives are set up only for As (6 ng/m<sup>3</sup>), Pb (500 ng/m<sup>3</sup>), Cd (5 ng/m<sup>3</sup>), and Ni (20 ng/m<sup>3</sup>) listed in 2008/50/EC and 2004/107/CE. This study compiled and compared the concentrations of 20 trace elements across seven countries. Figure 4.1.3 illustrates the concentration ranges for each trace elements, revealing that the average concentrations of As, Pb, Cd, and Ni all complied with EU standards.



**Figure 4.1.3.** Range of concentrations of 20 trace elements in the PM<sub>10</sub> size fraction across 55 European sites, considering the average for each site. Adapted from Liu et al. (2024).

The highest concentrations were recorded for Zn, Cu and Ti (40, 23 and 20 ng/m<sup>3</sup>, respectively), followed by Mn and Ba (12 and 11 ng/m<sup>3</sup>, respectively), all of them being conventionally attributed to brake-wear, tyre-wear and road dust resuspension in urban environments (Amato et al., 2016; Charron et al., 2019). Inhalation of these trace elements poses significant health risks. For instance, As, Cd, and Ni are known carcinogens, with exposure linked to lung and bladder cancers (Wu et al., 2022; Wang et al., 2023). Zn, Cu, and Mn, while essential in small amounts, can cause toxicity at higher concentrations, leading to respiratory and cardiovascular problems (Wu et al., 2019). Overall, the presence of these toxic metals in PM highlights the need for stricter regulatory measures and continuous monitoring to mitigate adverse health effects on urban populations.

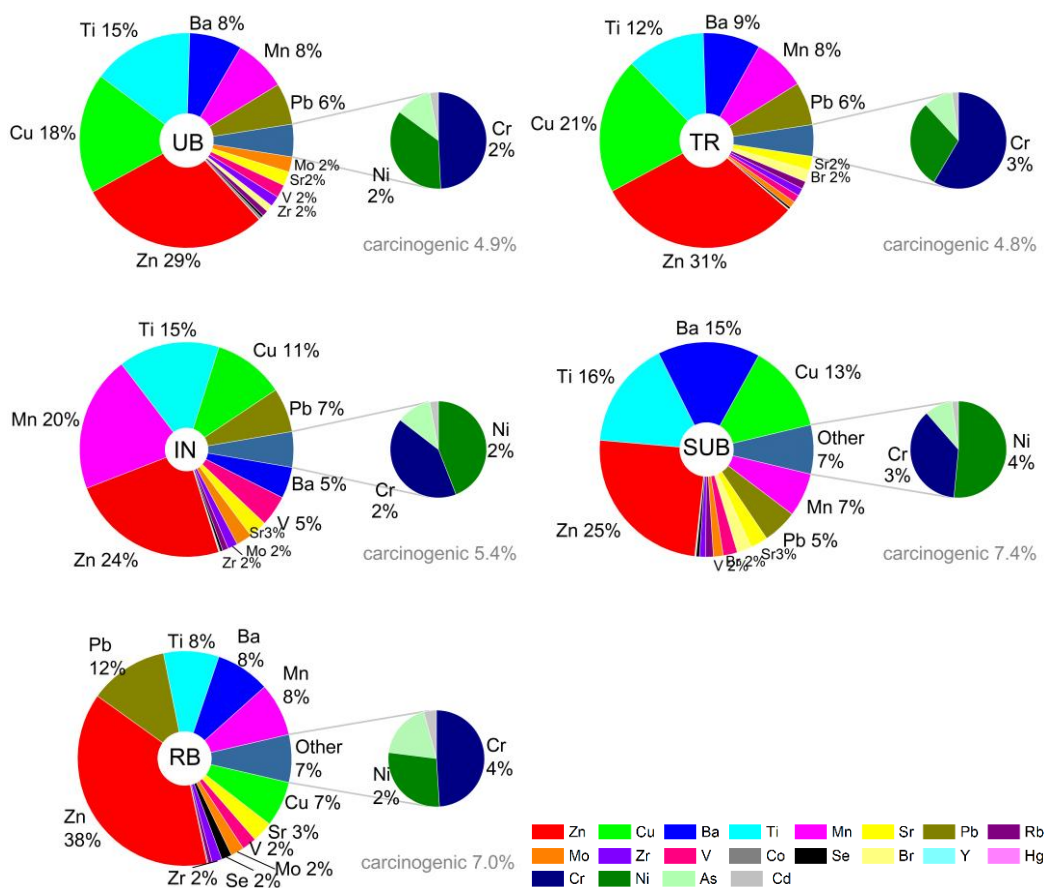
Table 4.1.1 shows the average concentration range of trace elements, considering the average for each site for the IND, TR, UB, SUB, and RB sites, for PM<sub>10</sub> and PM<sub>2.5</sub>. The ranges of the two PM sizes are not directly comparable because not many sites are reporting PM<sub>10</sub> and PM<sub>2.5</sub> data. However, the table might be used as a reference of the usual concentrations found in the different environments.

**Table 4.1.1.** Average concentration range of trace elements, considering the average for each site, in industrial (IND), traffic (TR), urban background (UB), suburban background (SUB) and regional background (RB) sites, in ng m<sup>-3</sup>, for PM10 and PM2.5. Data from Liu et al. (2024). ND, not determined.

	PM10					PM2.5				
	IN	TR	UB	SUB	RB	IN	TR	UB	SUB	RB
As	<0.1-10	<0.1-9.2	<0.1-7.9	<0.1-28	<0.1-4.1		0.2-0.7	<0.1-1.6	<0.1-0.4	
Ba	<0.1-61	<0.1-133	<0.1-416	<0.1-344	0.1-20		<0.1-6.7	<0.1-24.7	4.0-7.9	
Br	<0.1-2.3	<0.1-734	<0.1-160	<0.1-23	<0.1-3.0		ND	ND	ND	
Cd	<0.1-6.6	<0.1-5.2	<0.1-9.3	<0.1-7.0	<0.1-0.7		<0.1-0.2	<0.1-0.1	3.2-3.7	
Co	<0.1-2.7	<0.1-2.2	<0.1-47	<0.1-110	<0.1-0.2		<0.1-0.1	<0.1-0.1	<0.1-0.1	
Cr	<0.1-32	<0.1-51	<0.1-200	<0.1-122	<0.1-34		0.5-2.3	<0.1-2.9	0.8-1.3	
Cu	<0.1-349	<0.1-215	<0.1-1087	<0.1-117	<0.1-1.5		7.9-15	0.7-16.2	2.4-5.1	
Hg	<0.1-55	<0.1-216	<0.1-50	0.5-56	01-35.2		ND	ND	ND	
Mn	<0.1-118	<0.1-149	<0.1-185	<0.1-91	<0.1-28		2.1-7.8	0.1-3.8	2.0-3.3	
Mo	<0.1-46	<0.1-177	<0.1-57	<0.1-5.0	<0.1-0.1		<0.1-3.2	<0.1-16	<0.1-22	
Ni	<0.1-95	<0.1-261	<0.1-64	<0.1-318	<0.1-0.1		<0.1-0.9	<0.1-2.5	1.6-4.9	
Pb	<0.1-967	<0.1-312	<0.1-306	<0.1-149	<0.1-3.6		0.8-5.2	0.5-4.9	2.6-4.4	
Rb	0.1-15	<0.1-45	<0.1-35	<0.1-18	<0.1-8.1		0.2-1.3	0.1-1.3	0.5-0.9	
Se	<0.1-62	<0.1-32	<0.1-211	<0.1-57	0.1-119		<0.1-0.1	<0.1-0.1	0.4-0.5	
Sr	<0.1-92	<0.1-130	<0.1-147	<0.1-100	<0.1-1.8		<0.1-5.2	<0.1-16	0.7-1.5	
Ti	<0.1-516	<0.1-620	<0.1-345	0.1-521	<0.1-1.6		0.7-6.1	<0.1-0.1	3.3-10	
V	0.1-118	<0.1-34	<0.1-64	<0.1-23	0.2-4.7		0.1-0.3	<0.1-0.5	1.5-2.9	
Y	<0.1-2.8	<0.1-11	<0.1-7.6	<0.1-3.0	ND		<0.1-0.3	<0.1-0.3	ND	
Zn	<0.1-1034	0.1-575	<0.1-1983	<0.1-356	1.8-56		7.0-26	3.5-30	9.2-11	
Zr	<0.1-23	<0.1-23	<0.1-18	<0.1-10	ND		<0.1-5.2	<0.1-8.1	<0.1-11	

Additionally, the analysis of concentrations for these 20 trace elements in PM10 revealed varying proportions of non-carcinogenic and carcinogenic metals across different environments (Figure 4.1.4). Carcinogenic trace elements reach from 1% to 16% of the bulk trace element loads among all the study sites. Among carcinogenic trace elements, Cr (3 ±1 % of the bulk trace element loads) and Ni (2 ±2 %) are the ones with the highest contributions. On the other side, Zn (29 ±9 %), Cu (16 ±7 %), and Ti (14 ±8 %) dominated the non-carcinogenic trace element loads, followed by Ba (9 ±6 %), Mn (9 ±6 %), Pb (6 ±3 %) and Mo (2 ±3 %). These rankings remain consistent across environmental settings and countries. More specifically, the highest average concentrations were observed for Zn at TR and IN sites (45 ±46 and 41 ±64 ng/m<sup>3</sup>, respectively), Cu (39 ±25 ng/m<sup>3</sup>), Ti (26 ±30 ng/m<sup>3</sup>), Ba (17 ±16 ng/m<sup>3</sup>), Pb (13 ±19 ng/m<sup>3</sup>) at TR sites, and Mn (27 ±78 ng/m<sup>3</sup>) and Cr (6 ±4 ng/m<sup>3</sup>) at IN sites. Concerning the various countries, the maximum average concentrations were found for Zn in Portugal (54 ±40 ng/m<sup>3</sup>), Ti (33 ±11 ng/m<sup>3</sup>), Cu (28 ±29 ng/m<sup>3</sup>) and Pb (10 ±10 ng/m<sup>3</sup>) in Spain, and Cr (5 ±2 ng/m<sup>3</sup>) and Ni (4 ±5 ng/m<sup>3</sup>) in Italy. Additionally, at five RB monitoring sites in the UK, in which the mass of trace elements is moderately low, the proportion of carcinogenic elements reach relatively high proportions (8-15 % of total trace element mass concentrations).

Nevertheless, these concentrations were generally lower than those reported in China (Wang et al., 2013; Cheng et al., 2018; Jiang et al., 2019), South Korea (Roy et al., 2019), and India (Jena and Singh, 2017). In addition, the concentrations of these trace elements at sites in Spain (UB, IND, TR, RB) decreased by approximately one order of magnitude compared to the study by Querol et al. (2007) concerning trace elements concentrations in PM<sub>10</sub> during the 1995 to 2006 period, a decrease which can be mainly attributed to the implementation of industrial emission directives and the elimination of Pb from gasoline. According to the EEA (2023b), Cu emissions increased by 4% in the EU-27 between 1990 and 2021. The primary sources of these emissions are attributed to automobile tyre and brake wear, as well as industrial emissions (EEA, 2018). In any case, emission inventories for road traffic pollutants tend to yield lower shares than when the contributions to urban exposure is evaluated due to the proximity of road-traffic emissions to urban AQ monitoring sites and citizens. Many studies previously outlined the contributions of various emission sources to trace elements atmospheric concentrations. Industrial processes were identified as important contributors to As, Cd, Cu, Pb, Mn, and Zn (Allen et al., 2001; Marcazzan et al., 2001; Querol et al., 2007; Fernández-Camacho et al., 2012; Rodríguez-Espinosa et al., 2017). Ni and V were predominantly associated with oil combustion (Nriagu and Pacyna, 1988; Querol et al., 2007; Fernández-Camacho et al., 2012), while Cr was mainly associated with coal combustion and stainless-steel production (Pyle et al., 2001; Gao et al., 2002; Querol et al., 2007). Metal industry operations were also relevant sources for Mn, Zn, As, Pb, Co, and Cr (Querol et al., 2007; Fernández-Camacho et al., 2012; Pokorná et al., 2016). Additionally, soils and re-suspended dust played a significant role in Mn, Ni, V, Cu, and Ti emissions (Querol et al., 2007; Amato et al., 2009; Pant and Harrison, 2013; Amato et al., 2016; Squizzato et al., 2017). Municipal solid waste incinerators were important contributors to As, Cd, Cr, Cu, Hg, Pb, Mn, Ni, and V levels (Font et al., 2015; Ziegler et al., 2021). Vehicle exhaust also emerged as the primary source for trace elements, including Cu, Zn, Cd, Sn and Sb and Ba (Sternbeck et al., 2002; Schauer et al., 2006; Querol et al., 2007; Squizzato et al., 2017; Charron et al., 2019; Koc et al., 2024).



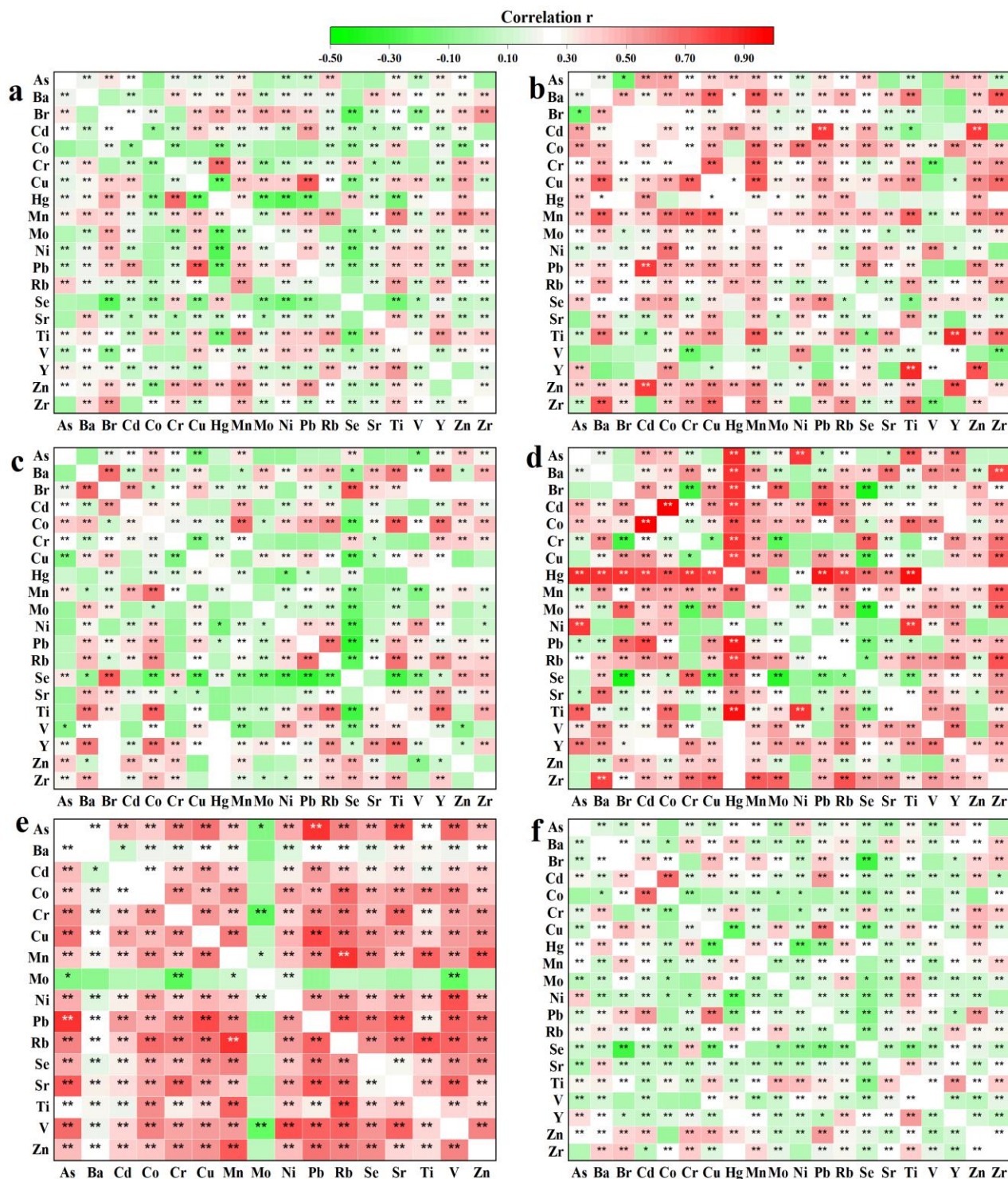
**Figure 4.1.4.** Proportions of various trace elements in different environments. Elements with mass fractions lower than 1.5% are not displayed, and the mass fractions of carcinogenic elements (Cr, Ni, As, and Cd) are given by the smaller pie charts. Adapted from Liu et al. (2024).

Therefore, determining particulate trace element emissions from diverse sources is essential for developing effective environmental management strategies. However, the dominance of specific trace elements in various RB regions can emphasise the need for targeted mitigation efforts tailored to the specific pollution profiles in these areas. For instance, at the DKI\_UI site, Mn and Zn accounted over 70% of the total trace elements, indicating the need to prioritise control measures for nearby industrial emissions. Specific source apportionment work will be addressed in the subsequent section, where detailed analyses and investigations into the origins of these trace elements was conducted. In any case traffic emissions are relevant in most cities, but not all of them have nearby metal smelters, cement factories, or city waste incinerators.

#### 4.1.1.4. Correlation analysis

The results of the cross-correlation analyses (Figure 4.1.5) show that many elements (10) are correlated at traffic sites, most probably because concentrations are mainly controlled by traffic

intensity, and even more at suburban and regional background site where mainly meteorology (advection, dispersion) controls basically all pollutant concentrations.



**Figure 4.1.5.** Correlations among trace elements in different environments including a, urban background; b, traffic; c, industry; d, suburban; e, rural background; and f, total data. (The lack of monitoring data for elements Br, Hg, Y, and Sr at rural background sites results in the exclusion of these elements from the elemental correlations analysis in e.). Adapted from Liu et al. (2024).

## 4.1.2. Major PM10 components

RI-URBANS compiled datasets of major PM components, including (including OC, EC, Na<sup>+</sup>, Mg<sup>2+</sup>, Al, K<sup>+</sup>, Ca<sup>2+</sup>, Fe, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) from 6 countries: France (24 sites), Italy (9), Spain (8), Switzerland (5), Portugal (3), and Greece (1) (Figure 4.1.1). Water-soluble ions (Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) were quantified using ion chromatographs (ICs). Al and Fe were measured simultaneously with the trace elements. OC and EC were analysed by a thermal-optical method using the EUSAAR\_2 protocol (Cavalli et al., 2010).

### 4.1.2.1. Concentrations of major PM10 components

Figure 4.1.6 shows the major PM10 constituent concentrations (OC, EC, Na<sup>+</sup>, Mg<sup>2+</sup>, Al, K<sup>+</sup>, Ca<sup>2+</sup>, Fe, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) at different environment types (UB, TR, IND, SUB, and RB).

In the UB sites, OC had an average concentration (of the averages of the sites) of 6.0±5.4 µg/m<sup>3</sup>, EC around 1.3±1.3 µg/m<sup>3</sup>, NO<sub>3</sub><sup>-</sup> 2.2±3.0 µg/m<sup>3</sup>, SO<sub>4</sub><sup>2-</sup> 1.8±1.4 µg/m<sup>3</sup> and NH<sub>4</sub><sup>+</sup> around 0.82±1.1 µg/m<sup>3</sup>. Median concentrations of Ca<sup>2+</sup>, Fe, Na<sup>+</sup>, Cl<sup>-</sup>, Al, K<sup>+</sup>, and Mg<sup>2+</sup> reached around 0.40±0.44, 0.40±0.40., 0.33±0.49, 0.30±0.70, 0.25±0.38, 0.18±0.24, and 0.04±0.05 µg/m<sup>3</sup>, respectively.

Overall, the concentration of major PM10 constituents varied across different environment types (Table 4.1.2), reflecting the influence of specific human activities and natural processes (Querol et al., 2004; Liu et al., 2023). Specifically, the concentrations of OC and EC were observed to be higher in UB, TR, UI, and SUB environments compared to RB areas (Figure 4.1.6), resulting from higher emissions from combustion sources (e.g. traffic, industries, and residential heating) at the formers (Flores et al., 2020; Tian et al., 2021). At RB sites, the OC/EC ratio is significantly higher than at other site types, reflecting the larger contribution to OC from both anthropogenic and biogenic SOA. Thus, a high proportion of OC has a regional origin, while EC is more local (traffic and biomass burning).

For metal ions and elements, the concentrations of Na<sup>+</sup>, Mg<sup>2+</sup>, Al, and Fe were higher at UI and TR environments due to industrial and vehicular emissions (Srimuruganandam and Nagendra, 2012; Jandacka et al., 2017). Intermediate concentrations were found in UB and SUB due to the influence of traffic and construction activities (Wu et al., 2020). In contrast, RB areas had lower metal ion and element concentrations, resulting from less industrial activity and lower traffic density. K<sup>+</sup> and Ca<sup>2+</sup> concentrations were higher in SUB, UB, and UI due to more biomass burning and construction activities compared to rural areas.

Chloride (Cl<sup>-</sup>) concentrations were higher in UI due to industrial processes, with intermediate levels in TR and SUB, and the lowest in RB.

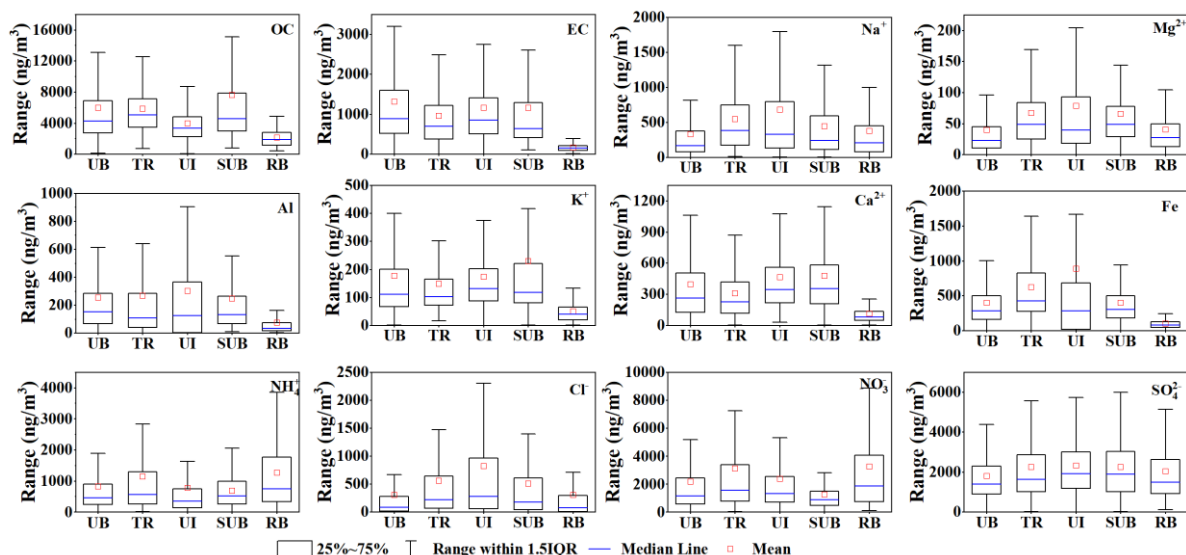
In terms of secondary inorganic compounds, SO<sub>4</sub><sup>2-</sup> concentrations did not show significant differences across environments, reflecting that SO<sub>4</sub><sup>2-</sup> is formed from the oxidation of SO<sub>2</sub>, and mainly produced by cloud processing, which is actually a large-scale process. NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations were higher in TR and RB most probably due to the proximity of the vehicle emissions and the high NH<sub>3</sub> concentrations found in some RB sites due to agriculture and farming emissions (Suarez-Bertoa et al., 2017; Hopke and Querol, 2022; Liu et al., 2024), respectively, with intermediate levels in UB and UI, and lowest in SUB.

Table 4.1.2 shows the average concentration range of major PM components, considering the average for each site for the IND, TR, UB, SUB, and RB sites, for PM10 and PM2.5. The ranges of the two PM sizes are not directly comparable because not many sites are reporting PM10 and PM2.5 data. However, the table might be used as a reference of the usual concentrations found in the different environments.

**Table 4.1.2.** Average concentration range of major PM components, considering the average for each site for industrial (IND), traffic (TR), urban background (UB), suburban background (SUB) and regional background (RB) sites, in µg m<sup>-3</sup>, for PM10 and PM2.5. Data from Liu et al. (2024). ND, not determined.

	PM10					PM2.5				
	IND	TR	UB	SUB	RB	IND	TR	UB	SUB	RB
OC	2.2-6.0	2.9-18*	2.1-19*	2.4-33*	1.8-2.3		1.9-4.3	1.0-4.9	2.7-5.4	
EC	0.7-2.1	0.3-4.6*	0.2-4.5*	0.4-3.9	0.2-0.2		0.6-1.4	0.2-1.2	0.3-1.1	
SO <sub>4</sub> <sup>2-</sup>	1.7-3.8	1.2-3.1	0.7-2.8	0.5-4.0	2.0-2.2		0.5-1.7	0.5-2.0	1.5-3.1	
NO <sub>3</sub> <sup>-</sup>	1.1-6.5	1.2-6.4	0.7-7.9*	0.7-5.4	3.0-3.2		0.1-5.1	0.1-6.9*	0.2-0.8	
NH <sub>4</sub> <sup>+</sup>	0.1-2.3	0.3-2.4	0.2-3.3*	0.1-1.7	1.2-1.3		0.4-1.9	0.5-2.4*	0.6-0.8	
Cl <sup>-</sup>	0.2-0.4	0.1-3.5	0.2-1.2	0.3-0.8	ND		0.01-0.1	<0.01-0.1	<0.01-0.1	
Na	0.4-1.3	0.1-2.0	0.1-0.9	0.2-0.8	ND		0.02-0.1	0.0-0.1	0.1-0.1	
Mg	0.2-0.4	0.1-0.4	0.0-0.9	0.1-0.4	ND		0.01-0.02	0.0-0.6	0.0-0.2	
Ca	1.7-2.7	0.3-1.2	0.2-1.6	0.2-0.8	ND		0.05-0.2	0.1-0.2	0.1-0.2	
Si	ND	0.3-1.3	0.2-1.3	0.2-1.0	ND		<0.05-0.1	0.1-0.7	0.1-0.3	
Al	0.1-1.3	0.1-0.8	0.0-1.1	0.0-0.6	0.1-0.1		<0.05-0.1	0.0-0.2	0.0-0.1	
Fe	0.3-3.9	0.3-1.4	0.1-1.2	0.0-1.1	0.1-0.2		0.1-0.5	0.0-0.2	0.1-0.1	
K	0.2-1.4	0.2-0.4	0.2-1.3	0.2-1.5	ND		0.1-0.5	0.0-0.6	0.1-0.2	
Levogluconan	0.1-0.3	0.2-0.8	0.1-3.2*	0.2-0.9	0.1-0.1		0.03-0.3	0.0-1.1	<0.1-0.3	

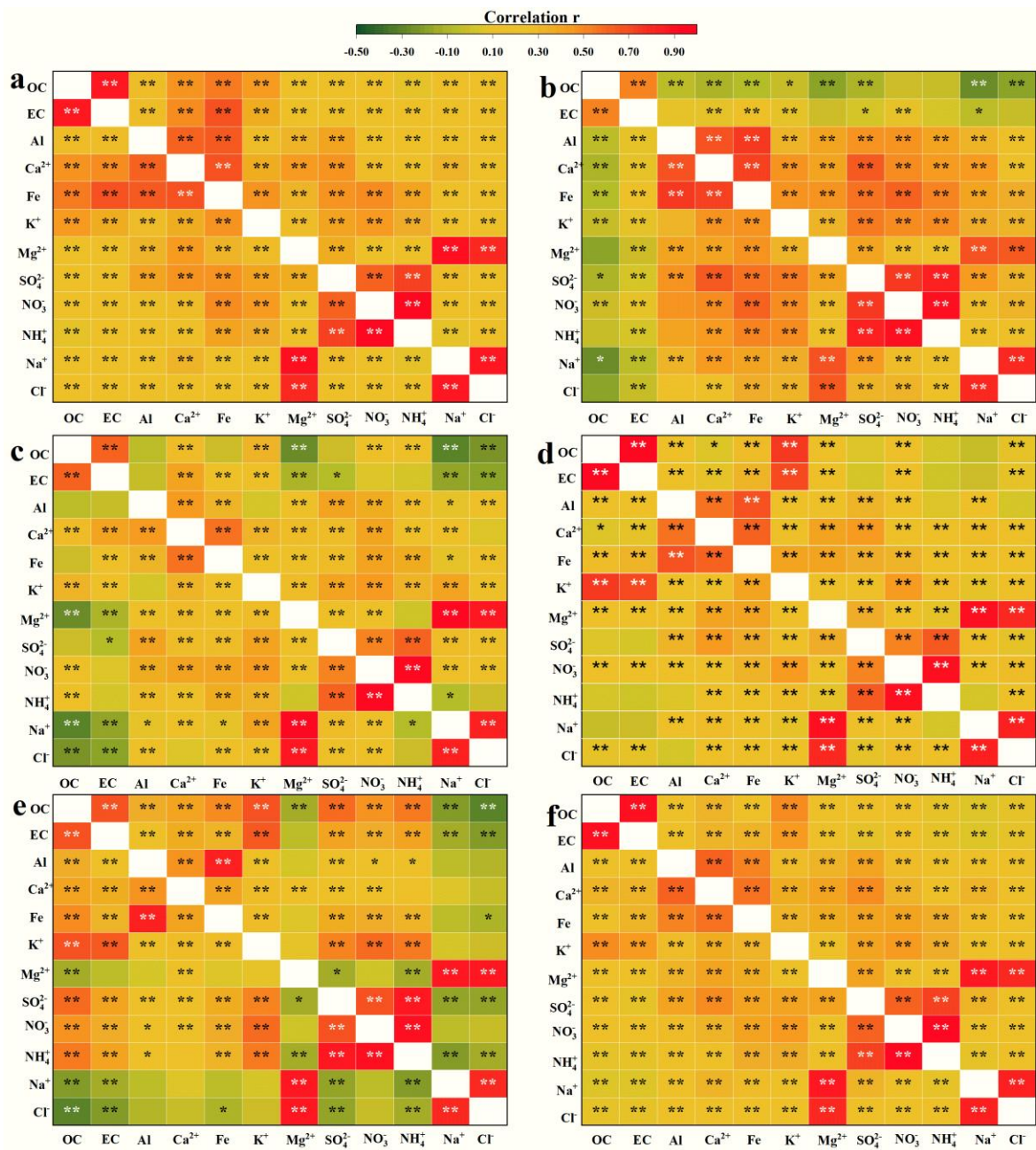
\* Highest values of the range are due to winter measurement campaigns



**Figure 4.1.6.** Concentrations of 12 major PM<sub>10</sub> constituents at different types of monitoring sites across Europe (UB, urban background; TR, traffic; UI, urban industry; SUB, suburban, and RB, rural background). Unpublished data.

#### 4.1.2.2. Correlation analysis for major PM<sub>10</sub> constituents

Figure 4.1.7 illustrates the correlations among major constituents at various locations, revealing distinct correlation patterns across different sites. Similarly, to trace elements, major PM constituents generally exhibited significantly strong correlations ( $p < 0.01$ ), particularly OC vs. EC, Fe vs. Al, and among the inorganic ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ). This indicated several important aspects. Firstly, the strong correlation between OC and EC typically indicates a common source, such as combustion processes, including biomass burning and fossil fuel combustion (Salma et al., 2017; Salma et al., 2020).



**Figure 4.1.7.** Correlations among major PM10 constituents (OC, EC, Al, Ca<sup>2+</sup>, Fe, K<sup>+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup>) in different environments including a, urban background; b, traffic; c, industry; d, suburban; e, rural background; and f, total data.

The correlation between Fe and Al suggests they predominantly originate from crustal sources, such as crustal mineral dust (Prospero et al., 2001; Zhang et al., 2009). Secondly, the strong correlations among inorganic ions suggest these ions undergo similar atmospheric chemical processes, such as secondary aerosol formation (Squizzato et al., 2013; Xue et al., 2014) and mixing processes. Thirdly, the differences in correlation patterns across various environments reflected differences in pollution source strengths and processes. Urban areas showed stronger OC and EC correlations,

reflecting the predominance of primary OC. Rural areas are typically more influenced by natural sources, such as soil dust suspension, leading to higher correlations between crustal elements like Fe and Al. Lastly, the correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  can indicate the presence of sea salt aerosols (Mihajlidi-Zelić et al., 2006; Manders et al., 2010), and the correlation between  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  to secondary aerosol formation (Walker Jr, 2005; Lawal et al., 2018). Overall, correlation analyses may provide a deeper understanding of the sources and behaviour of atmospheric pollutants, enabling to identify and control pollution sources for protecting the environment and public health.

## 4.2. Online PM speciation: non-refractory compounds

### 4.2.1. Introduction

PM sources vary with location and types of sites, but the most common ones are biomass burning, road traffic, secondary aerosol formation, sea salt and road dust suspension, cooking, shipping, etc. (Amato et al., 2016; Chen et al., 2022; Titos et al, 2014; Vecchi et al, 2008). In comparison to offline PM chemistry measurements, online techniques usually provide higher time resolution, making them more suitable for e.g. acute air pollution episode management.

PM source apportionment from on-line chemical speciation has been performed from the release of the first online mass spectroscopy instrument, the Aerosol Mass Spectrometer in 2007 (Aerodyne Inc., Billerica, US, Canagaratna et al., 2007). Posteriorly, longer term source apportionment studies have been enabled with the release of the Aerosol Chemical Source Monitor (Ng et al., 2011; Fröhlich et al, 2013), which requires significantly less user intervention and for longer deployments. In turn, source apportionment studies using online metals measurements have been carried out from Xact 625i measurements for several years.

However, source apportionment by receptor modelling is a methodology which implies certain user decisions based on previous studies and site knowledge. Also, the model-guidance techniques which users may decide to apply can substantially influence the results (Via et al., 2022). Moreover, the same sources found at one site or another can be legitimately quite different in composition due to slightly different origin characteristics (Chen et al., 2022). As a consequence, source apportionment studies are difficult to harmonise and intercompare, unless harmonised best practices are available. This document presents the comparison of online PM<sub>1</sub> speciation datasets from 55 sites all over Europe acknowledging the limitations of such studies and the difficulties encountered. These sites

are located in France (13 sites), Italy (3), Spain (3), Switzerland (2), UK (4), Greece (2), Cyprus (1), Czech Republic (1), Estonia (1), Finland (1), Ireland (1), Lithuania (1), Poland (1) and Romania (1).

## 4.2.2. Methodology

### 4.2.2.1. Non-refractory-PM1 data compilation

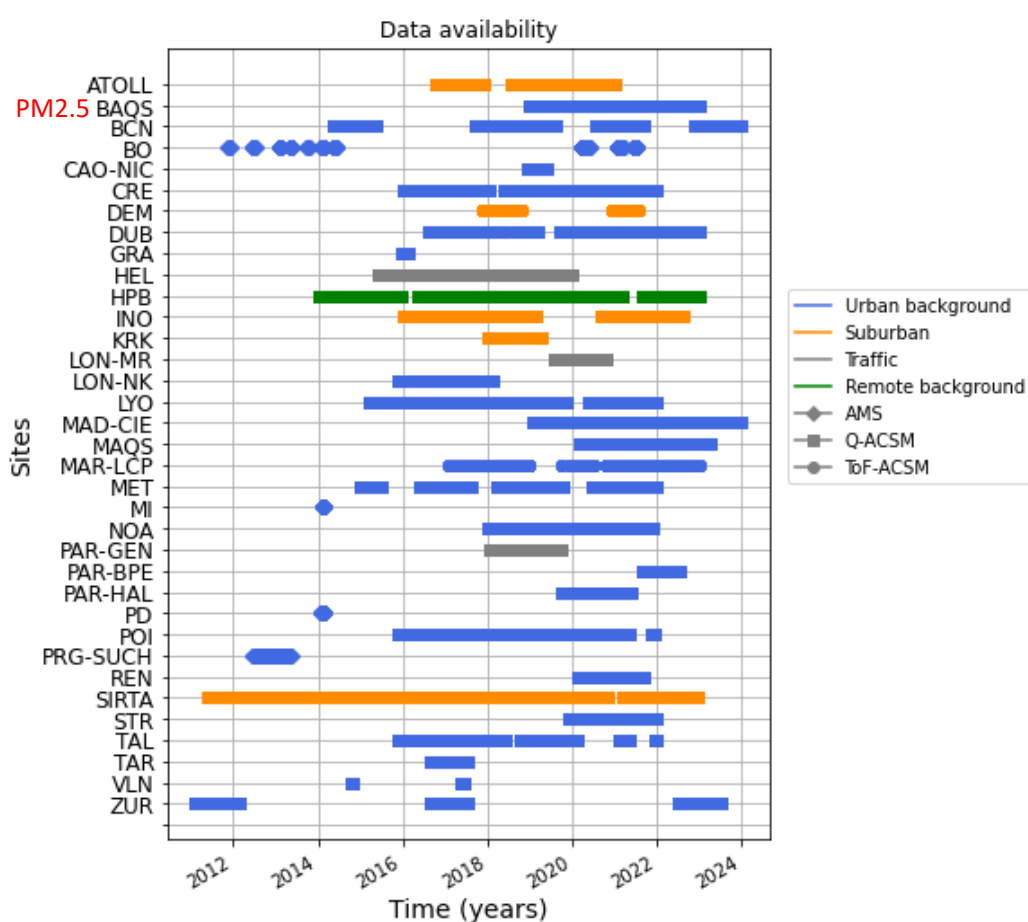
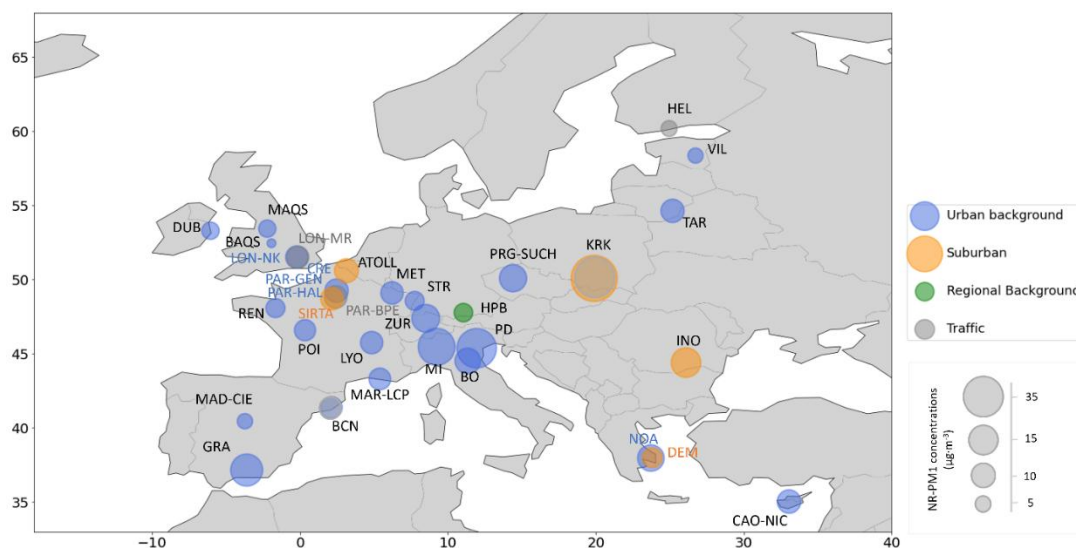
The comparison of the NR components of PM1 has included data ranging from 2011 to 2023 provided to RI-URBANS by AQMNs, research infrastructures (such as ACTRIS) and single research institutes (see Figure 4.2.1 and Table 4.2.1), from:

- 26 Urban background (UB) sites: Birmingham (BAQS), Barcelona-Palau Reial (BCN), Bologna (BO), Cyprus Atmospheric Observatory (CAO-NIC), Creil (CRE), Dublin – UCD (DUB), Granada (GRA), London – North Kensington (LON-NK), Lyon (LYO), Madrid-CIEMAT (MAD-CIE), Manchester (MAQS), Marseille-Longchamp (MRS-LCP), Metz (MET), Milano Pascal (MI), Athens - Thissio (NOA), Paris Gennevilliers (PAR-GEN), Paris-Les Halles (PAR-HAL), Padova Granze (PAD), Poitiers (POI), Prague-Suchdol (PRG-SUCH), Rennes (REN), Strasbourg (STR), Talence (TAL), Tartu (TAR), Vilnius (VLN) and Zurich – Kazerne (ZUR).
- 5 Suburban (SU) sites: Lille (ATOLL), Athens-Demokritos (DEM), Magurele – Bucharest (INO), Krakow – AGH University (KRK), Gif-sur-Yvette (SIRTA).
- 3 Traffic (TR) sites: Helsinki (HEL), London – Marylebone (LON-MR), Paris – Boulevard Périphérique Est (PAR-BPEst)
- 1 Remote background (RB) site: Hohenpeissenberg (HPB). This site is used in order to compare the urban sites to a non-urban one of high data coverage.

The COVID-19 lockdown period was included at some sites (Figure 4.2.1b). The instruments used were the Quadrupole (Q) or Time of Flight (ToF) aerosol chemical speciation monitors (ACSM), or Aerosol Mass Spectrometers, with standard or capture vaporisers depending on the instrument size range (PM<sub>1</sub>, PM<sub>2.5</sub>, respectively), as listed in Table 4.2.1. The main difference in data collection between Q and ToF detectors is the measurement time resolution, usually of 30 min and 10 min, respectively. However, some sites did not comply with this general rule and adjusted it for the sake of measurement quality (Table 4.2.1).

**Table 4.2.1.** List of sites supplying non-refractory-PM1 measurements (inlet cut-off PM2.5 in BAQS) to the current review with location, type of instrumentation, time resolution, and additional measurements of PMF inputs and outputs availability. Q: Q-ACSM; ToF: ToF ACSM. SU: suburban; UB: urban background; TR: traffic site. From Chen et al., 2022.

Site	Acronym	Type	Lat	Lon	Alt	Type	Time Res.	PMF input	PMF output
Lille	ATOLL	SU	50.61	3.14	70	Q	30'	Y	Y
Birmingham (PM2.5)	BAQS	UB	52.46	-1.93	143	Q	1h	Y	N
Barcelona	BCN	UB	41.39	2.118	80	Q	30'	Y	Y
Bologna	BO	UB	44.52	11.34	0	Q	5'	Y	Y
Nicosia	CAO-NIC	UB	35.04	33.06	352	Q	30'	Y	Y
Creil	CRE	UB	49.26	2.47	31	Q	30'	N	N
Athens-Demokritos	DEM	SU	38	23.82	270	ToF	30'	Y	Y
Dublin – UCD	DUB	UB	53.31	-6.05	35	Q	30'	N	Y
Granada	GRA	UB	37.16	-3.61	68	Q	30'	N	Y
Helsinki	HEL	TR	60.20	24.95	25	Q	30'	N	N
Hohenpeissenberg	HPB	RB	47.8	11.0	985	Q	5'	N	N
Magurele – Bucharest	INO	SU	44.41	26.09	93	Q	30'	Y	Y
Krakow - AGH Univ.	KRK	SU	50.09	19.89	13	Q	30'	Y	Y
London - Marylebone Road	LONMR	TR	51.52	-0.15	39	Q	30'	Y	Y
London - North Kensington	LONNK	UB	51.52	-0.21	27	Q	30'	Y	Y
Lyon	LYO	UB	45.76	4.85	160	Q	30'	N	N
Madrid – CIEMAT	MAD	UB	40.46	-3.73	669	Q	30'	N	N
Manchester	MAQS	UB	53.44	-2.21	43	Q	30'	N	N
Marseille	MAR-LCP	UB	43.31	5.395	71	ToF	10'	Y	Y
Metz	MET	UB	49.11	6.22	204	Q	30'	N	N
Milano Pascal	MI	UB	45.48	9.234	118	AMS	5'	Y	Y
Athens – Thissio	NOA	UB	37.97	23.72	105	Q	30'	Y	N
Paris – BPEst	PAR-BPE	TR	48.84	2.413	48	Q	30'	N	N
Paris – Gennevilliers	PAR-GEN	UB	48.93	2.295	28	Q	30'	N	N
Paris - Les Halles	PAR-HAL	UB	48.86	2.345	35	Q	30'	N	N
Padova Granze	PD	UB	45.38	11.94	11	AMS	30'	N	Y
Poitiers	POI	UB	46.59	0.34	71	Q	30'	N	N
Prague – Suchdol	PRG-SUCH	UB	50.1	14.4	277	AMS	30'	Y	N
Rennes	REN	UB	48.09	-1.66	45	Q	30'	N	N
Gif-sur-Yvette	SIRTA	SU	48.71	2.15	163	Q	30'	N	N
Strasbourg	STR	UB	48.57	7.753	140	Q	30'	N	N
Talence	TAL	UB	44.80	-0.59	23	Q	30'	N	N
Tartu	TAR	UB	58.37	26.73	39	Q	1h	N	Y
Vilnius	VLN	UB	54.64	25.18	162	Q	30'	Y	Y
Zurich – Kaserne	ZUR	UB	47.4	8.5	409	Q	15'	Y	Y



**Figure 4.2.1.** (top) Location of the cities supplying data on non-refractory-PM1 (PM2.5 in BAQs) measurements for the present review. Size of the markers indicates non-refractory-PM1 average mass concentrations, and colour indicates the type of site. (bottom) Temporal measurement availability and type of instrument and site; UB Urban Background; TR, traffic; SUB, Suburban background.

### 4.2.3. Levels of non-refractory-PM1 mass concentrations

NR-PM1 mean concentrations amongst the European sites listed in Table 4.2.1 ranged from 1.9 to 366  $\mu\text{g m}^{-3}$  with an average of  $10.7 \pm 6.9 \mu\text{g}\cdot\text{m}^{-3}$  (one standard deviation). However not all the sites reach the annual coverage, and in some cases winter measurements were carried out. In the lower range, Birmingham, Tartu and Helsinki present mean concentrations below 5  $\mu\text{g m}^{-3}$ . This value is unexpectedly low for Birmingham, considering both the city population and the use of a PM2.5 cut-off inlet. Hence, the data from this site will be only used for pattern acknowledgement and relative composition with caution.

Regarding NR-PM1 composition, the main component was OA at all sites except Milano (39% of OA and 40% of  $\text{NO}_3^-$ ), which refers to January-February only.

The average, standard deviation, and ranges (average  $\pm$  standard deviation, min % - max %) of each species (for a set of sites excluding BAQS (PM2.5 instead of PM1) and without stations with less than one year as data coverage, excluded: CAO-NIC, GRA, MI, PD, PRG-SUCH, TAR, VLN) were:

- OA:  $55 \pm 10\%$ , 40-67%.
- $\text{SO}_4^{2-}$ :  $18 \pm 8\%$ , 9-48%
- $\text{NO}_3^-$ :  $16 \pm 5\%$ , 6-26%
- $\text{NH}_4^+$ :  $10 \pm 3\%$ , 5-19%
- Cl:  $1 \pm 1\%$ , <0.1-6%

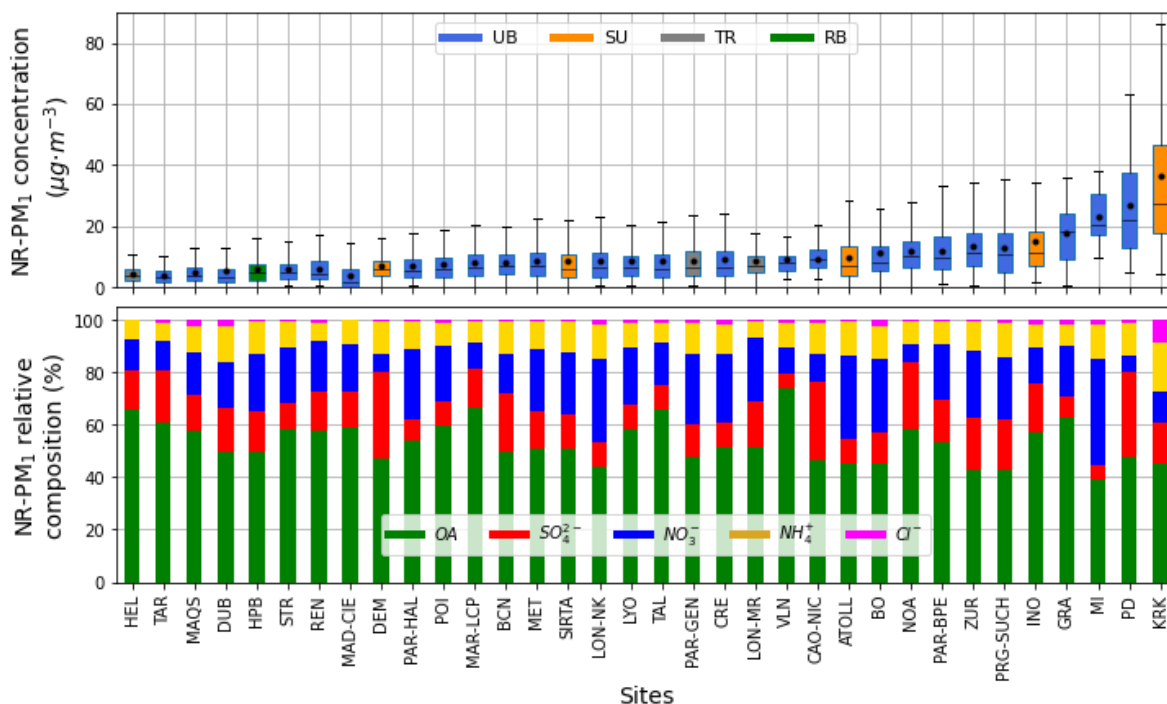
The 35 sites can be classified in four big groups according to the chemical compositions shown in Figure 4.2.2 at the bottom.

- $\text{SO}_4^{2-} \ll \text{NO}_3^-$ : Typically, continental or high-latitude sites, where winter stagnation episodes are frequent and/or severe, or with high traffic influence. Sites belonging to this group were: MAQS, STR, REN, DUB, MAD-CIE, DEM, PAR-HAL, POI, MET, SIRTA, LON-NK, LYO, TAL, PAR-GEN, CRE, LON-MR, VLN, ATOLL, BO, PAR-BPE, IPR, GRA, MI.
- $\text{SO}_4^{2-} \gg \text{NO}_3^-$ : Typically, with sea influence and in lower latitudes, where  $\text{SO}_4^{2-}$  is photochemically produced from DMS and/or shipping emissions. Sites belonging to this group were: TAR, DEM, MAR-LCP, BCN, CAO-NIC, NOA, PD.
- $\text{SO}_4^{2-} \approx \text{NO}_3^-$ : Typically, intermediate sites, where concentrations are similar in summer and winter. Sites belonging to this group were: HEL, DUB, PRG-SUCH, ZUR, INO.

- High Cl<sup>-</sup>: High concentration of chloride found in Krakow (period mean of 3.1  $\mu\text{g m}^{-3}$ ), the most polluted site, related to coal burning (Tobler et al., 2021).

Further discussion on OA concentrations will be carried out in section 3.3.4.

There was an area of particularly high concentrations, the Po valley, where the sites of Padova, Milano and Bologna. These three datasets presented very high NR-PM<sub>1</sub> concentrations and high amounts of NO<sub>3</sub><sup>-</sup>, with exception of Padova which is closer to the coast and more SO<sub>4</sub><sup>2-</sup> dominated. These results can be biased because Padova and Milano data is only for winter, but in any case, the Po valley is known as a European hotspot for PM accumulation due to the orographic and meteorological conditions, multiple sources of PM and recirculating breeze regimes which cause severe winter pollution episodes (Scotto et al., 2021).



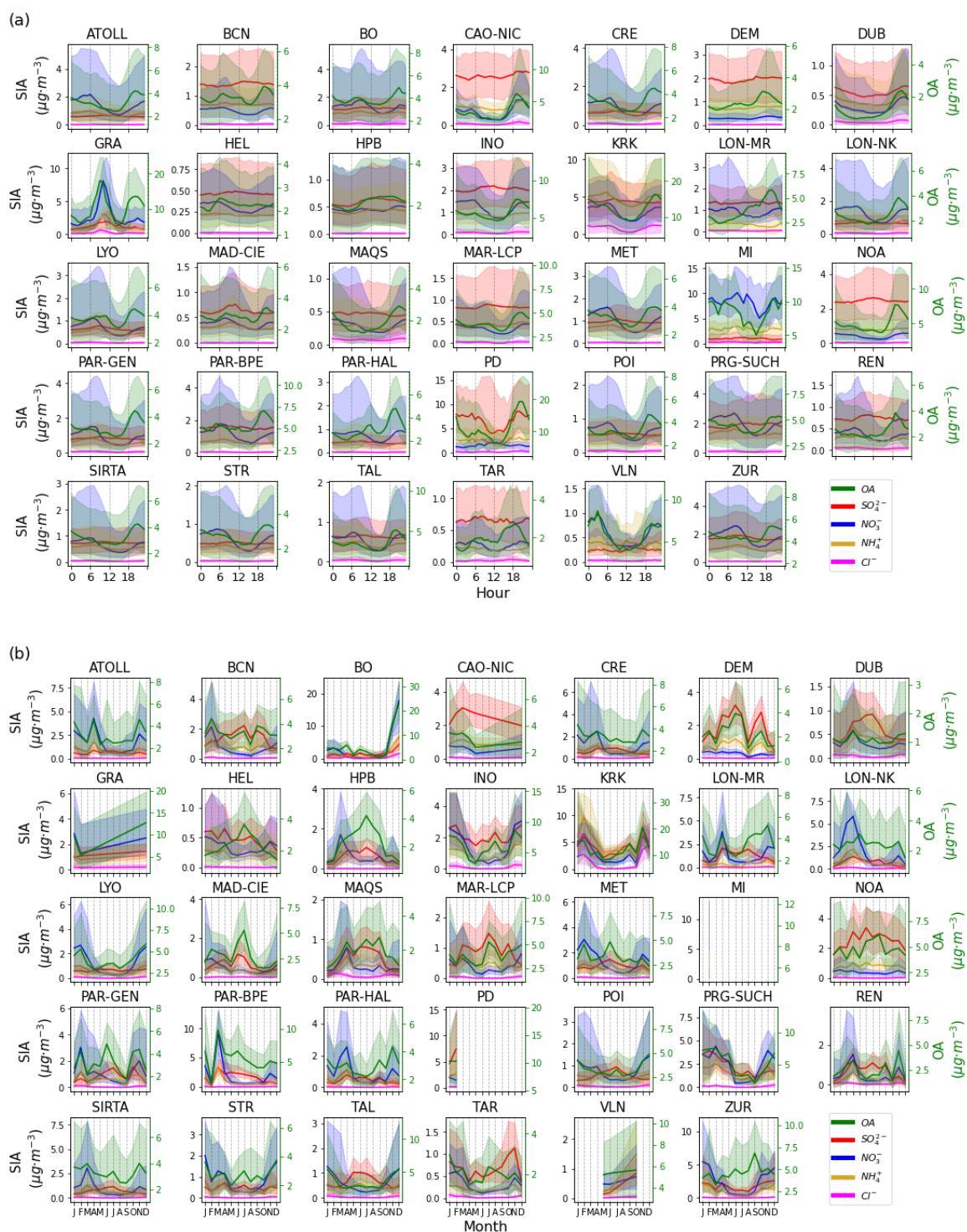
**Figure 4.2.2.** (a) NR-PM<sub>1</sub> concentrations boxplots. (b) Relative composition of NR-PM<sub>1</sub> compounds. Both graphs are ordered by growing mean concentration of NR-PM<sub>1</sub>. Concentration boxplots include average (circle), median and quartiles 25 and 75%. (Lower) Relative composition of NR-PM<sub>1</sub> (PM<sub>2.5</sub> in BAQS) compounds. Both graphs are ordered by growing mean concentration of non-refractory-PM<sub>1</sub>.

#### 4.2.3.1. *Diel and seasonal patterns*

Diel and monthly cycles are plotted for all sites and all constituents in Figure 4.2.3.

There were two main types of OA diel cycles, one presenting a deep decrease during the central hours of the day and increasing at the evening (ATOLL, DUB, LON-NK, NOA, REN, SIRTA, STR, MAQS, etc.) and the other presenting a peak around 6-10 am (BCN, BO, GRA, HEL, MAD-CIE, PAR-HAL, TAR). The behaviour of the first group was likely induced by meteorological conditions, due to the development of the boundary layer at the central hours of the day, which dilutes pollution in the troposphere and reduces pollutant concentrations. The morning peak of the second group denoted the presence of traffic-related OA (Hydrocarbon-like OA, HOA) during the morning road traffic rush hours. Nitrate diel cycles usually present this road traffic peak as well, due to the fast conversion of traffic-emitted  $\text{NO}_x$  to particulate  $\text{NO}_3^-$ . The diel cycle of  $\text{SO}_4^{2-}$  was rather flat with a slight increase during noon. This can be due to i) the volatilisation of semi volatile OA and ammonium nitrate and/or (ii) in-situ formation of  $\text{SO}_4^{2-}$  from  $\text{SO}_2$  reaction with OH in summer.  $\text{NH}_4^+$  and  $\text{Cl}^-$  cycles were rather flat and noisy throughout the day.

Regarding seasonal variations, OA also behaved differently at the various sites. At e.g., BO, CRE, DUB, PRG-SUCH, and TAL, the highest concentrations occurred in the winter months, probably related to the severe winter stagnation episodes and an additional biomass burning OA source (BBOA). However, for some other sites (e.g., ZUR, MAD-CIE, STR, MAQUS, MET, DEM), there was a significant increase of OA in the summer months as a consequence of the increased secondary OA production due to the higher solar irradiation which boosts photochemistry.  $\text{SO}_4^{2-}$  presented a significant increase in warm periods likely due to an increase of  $\text{SO}_4^{2-}$  formation through DMS or  $\text{SO}_2$  oxidation in photochemistry-enhanced conditions, and/or a higher shipping (cruises) activity in summer (Pérez et al., 2016; in 't Veld et al., 2021).  $\text{NO}_3^-$  concentrations presented the opposite cyclicity, with a relevant minimum in summer, related to the instability of  $\text{NH}_4\text{NO}_3^-$  in high-temperature conditions.  $\text{NH}_4\text{Cl}$  is also unstable at high-temperature, so  $\text{Cl}^-$  monthly cycles resembled those of  $\text{NO}_3^-$ . Mainly linked to  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  concentrations presented a decrease in summer, probably primarily due to the volatilisation of ammonium nitrate.



**Figure 4.2.3.** Non-refractory-PM1 compounds diel (a) and monthly (b) cycles. The averaged concentrations amongst all sites are represented in solid lines and the standard deviations in shaded areas. The secondary inorganic aerosol (SIA) compounds concentrations are plotted on the left axis (black) and OA concentrations are plotted in the right axis (green axis) for the sake of plot readability. Diel cycles time is in UTC.

### 4.3. Online PM speciation of trace elements and metals

High-time resolution trace element datasets obtained by using Xact 625i instruments were gathered across Europe. The data were provided by air quality monitoring networks and single research institutes involved in the ROXI WG. This collection consists of datasets from 17 Xacts deployed across multiple sites in Europe from 2018 to 2023. The datasets included measurements of 25 to 40 elements conducted with either an automated alternative inlet system switching between PM<sub>10</sub> and PM<sub>2.5</sub> samples, or unique PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> inlets. These sites were classified according to several typologies: 10 UB, 3 IND, 1 TR, 1 rural and 1 RB. Important information might be obtained by analysing these existing element measurement data at European urban sites, and particularly by comparing the concentration levels, the seasonality and the diel variations of these concentrations across Europe. This overview is an ongoing work that will be presented in a future dedicated article and thus will not be included in the current document.

## 5. RECOMMENDATIONS AND MAIN FINDINGS

### 5.1. Recommendations on measurements, quality control and data management

#### 5.1.1. Offline PM speciation

##### 5.1.1.1. Offline measurements of the PM components

The new EU AQ Directive (NAQD, CEU, 2024) requires or recommends the analysis of specific PM<sub>10</sub> and PM<sub>2.5</sub> constituents, such as metals (As, Cd, Ni, Pb), polyaromatic hydrocarbons (PAH), levoglucosan, elemental and organic carbon (EC and OC), SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>. The aim of this complete chemical characterisation is to “*assess the possible contribution from long-range transport of pollutants, support source apportionment analysis and for the understanding of specific pollutants such as particulate matter*” (CEU, 2024).

In order to ensure that the information collected on PM speciation is comparable and sufficiently representative across the European Union, it is important that standardised measurement techniques and common criteria are used for the assessment of ambient AQ. To this end, standard

sampling and analytical protocols, including criteria for QA/QC, are listed in the NAQD, and these standards need to be followed:

- EN12341:2023 sets the procedure for the determination of the PM<sub>10</sub> or PM<sub>2.5</sub> mass concentration of suspended particulate matter.
- EN14902:2005 describes the standard method for the measurement of Pb, Cd, As and Ni in the PM<sub>10</sub> fraction of suspended particulate matter.
- EN15549:2008 standardised the method for the measurement of benzo[a]pyrene concentration in the PM<sub>10</sub> fraction of suspended particulate matter.
- EN16913:2017 describes the standard method for the measurement of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> in PM<sub>2.5</sub> deposited on filters.
- EN16909:2017 is the European standard for the measurement of elemental carbon (EC) and organic carbon (OC) in PM<sub>2.5</sub> collected on filters.

The aforementioned standards do not cover all the constituents of interest for a comprehensive characterisation of PM. The measurement of additional PM inorganic and organic constituents might be required for an advanced AQ management, including source apportionment for cost-effective action plans, epidemiological and toxicological analyses to identify the most harmful PM components and their sources, and climate-relevant information on PM, among others.

For instance, source apportionment studies also require the measurement of specific metals, such as e.g. Al, Ca, Fe, V, Sb, Sn, Zn as tracers of soil dust and different industrial, traffic and combustion sources, and organic molecules (e.g., PAHs, sugars) as tracers of biomass burning, on top of the species listed in the NAQD (Amato et al., 2024). This enables to identify most of the major contributors to PM in Europe. For determining more specific sources, it can be needed to measure also MSA, oxalate, and polyhydric alcohols, among others.

According to the aforementioned standards, the determination of these PM constituents shall be performed after PM collection using PM<sub>10</sub> and/or PM<sub>2.5</sub> samplers complying with the requirements of EN12341:2023, i.e. using low-volume (2.3 m<sup>3</sup> h<sup>-1</sup>). This limits the mass of PM collected and makes it difficult to perform all the analyses required in a single filter if analyses of non-regulated PM constituents of interest are required. Using 2-3 low volume samplers, with different filters depending on the analytical technique to be subsequently used, would enable a complete chemical characterisation of each PM fraction. However, the use of high-volume samplers

( $\geq 30 \text{ m}^3 \text{ h}^{-1}$ ) and adequate filters can be considered for a complete chemical characterisation of PM, as long as equivalence with the European standard EN12341:2023 can be demonstrated.

EN16909:2017 standardises the measurement of airborne EC and OC in PM<sub>2.5</sub> deposited on filters. The CEN WG35 is currently evaluating the possibility to extend this standard to the determination of EC and OC in ambient PM<sub>10</sub>, and proposed guidance to test the equivalence of automated, (semi) real-time methods used to measure OC and EC with the European standard EN16909:2017. ACTRIS requires to follow the CEN standard and provides additional recommendation on top of EN16909 (<https://www.actris-ecac.eu/actris-gaw-recommendation-documents.html>).

The concentrations of major and trace elements in PM can be determined by X-Ray methods (as XRF and PIXE) or by atomic spectrometry-based techniques (ICP-MS and ICP-OES).

- XRF has relatively high LODs and LOQs for tracers of interest for source apportionment studies such as As, Cd, Sb, Se, Sn, among others. PIXE has lower LODs than XRF, but requires more complex instrumentation, making it more expensive and difficult to use routinely.
- ICP-MS and ICP-OES require acid digestion, are time consuming and more expensive, but LODs are very good for more than 50 elements. The acid digestion protocol recommended in EN14902:2005, does not allow the complete digestion of silicon-containing compounds and specific oxides, and therefore does not permit to quantify tracers of specific sources such as non-vehicle exhaust, road dust, and desert dust. For this purpose, it is recommended to perform a complete acid digestion using a HF:HNO<sub>3</sub>:HClO<sub>4</sub> mixture.

For the analysis of organic PM constituents, an overall standardised methodology is currently lacking, and only exists for PAHs, and more specifically for benzo[a]pyrene (EN15549:2008). Within ACTRIS, the Organic Tracers and Aerosol Constituents – Calibration Centre (OGTAC-CC) has been set-up to support and serve the determination of particulate organic tracer mass concentrations, as an additional chemical aerosol in-situ variable. ACTRIS OGTAC-CC and RI-URBANS are currently developing technical requirements and measurement guidelines as a basis to develop standard operating procedures (SOP) for different modules of organic marker compounds. In any case this document includes a review of existing methodologies and proposed strategies for those organic markers that lack reference methodologies, including primary organic aerosol markers (polycyclic aromatic hydrocarbons, anhydrous-monosaccharides, and saccharides) and secondary organic aerosol markers.

#### 5.1.1.2. *Data management*

According to EU legislation, the member states are obliged to submit the data to the European Air Quality Portal (EAQP) run by the European Environmental Agency (EEA). However, some guidance on how to do the data management locally within the AQMNs is needed, and will be provided by EEA. Also, it is needed to clarify what will be the situation for the measurements at supersites within the NAQD? Do the member states need to send the data to EAQP from the EEA as it is the case for other air pollutants? Probably the later will be the AQ option. If this is the case, it is recommended to the EAQP to follow the data management and templates from EBAS protocols. The EBAS protocols were established by EBAS in collaboration with EMEP and ACTRIS infrastructures.

#### 5.1.2. **Online PM speciation**

Online PM speciation with <1 h resolution can be of high interest to yield information to assess short-term policy decisions, i.e., during pollution episodes.

##### 5.1.2.1. *Measurement of the PM non-refractory components*

The Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) is the most widely used instrument for measurement of NR-PM1 (or PM2.5) components. It provides the ambient concentration of the following NR species: organic aerosol (OA),  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$  at a time resolution of about 15 to 30 min depending on the ACSM model. Sources of organic aerosols are identified by applying the positive matrix factorisation (PMF) receptor model to the organic mass spectra.

CEN standards are not available for these online methods. Recommendations are listed in Section 3.2.2. Detailed guidelines on instrument operation and maintenance, and on data treatment were produced by the COST-COLOSSAL Action and by ACTRIS-ERIC, and are available at [ACTRIS-ECAC website](#) (COST-COLOSSAL, 2021 and COST-COLOSSAL/ACTRIS, 2022).

The operation of ACSMs entails the usage of different software for the Q-ACSM (ACSM DAQ + ACSM local, ACSM Pumps Stats and Dryer stats, for ACSM data acquisition and data curation, respectively), and for the ToF-ACSM (Acquility and Tofware 3 for data acquisition and curation, respectively). The correct configuration of ACSM acquisition software is required to ensure the valid operation of the instrument.

Maintenance and quality control operations are complex and shall be carried out by trained staff. ACSM calibration is to be performed every 3-6 months and every time the instrument is relocated to ensure proper functioning.

All instruments are expected to participate in the ACTRIS annual intercomparisons for at the Aerosol Chemical Monitor Calibration Centre (ACMCC, Gif-sur-Yvette) at least every three years. In these intercomparison exercises, all participants' ACSM are calibrated and operated under the same conditions as those used during sampling, retrieving hence information of representative instrumental performance.

#### 5.1.2.2. *Measurement of trace elements and metals*

The most common commercially available instrument that provide users with continuous, near-real-time metals and trace element concentration measurements is the Xact 625i Ambient Metals Monitor, developed by Cooper Environmental Services (Sailbri Cooper Inc., Tigard, OR, USA). Other instruments exist, such as the Atmospheric Heavy Metals On-line Analyser EHM-X100 (Skyray Instrument Ltd., China) or the Particulate Monitor with X-Ray Fluorescence PX-375 (Horiba Ltd., Japan), though these are currently used to a much lesser extent in Europe.

The Xact instrument has been deployed at several monitoring stations in Europe and simultaneously measures up to 67 elements with an atomic number between aluminium (Al) and uranium (U). The measurement is based on reel-to-reel filter tape sampling followed by non-destructive X-Ray fluorescence (XRF) analysis of elements in the resulting particulate matter (PM) deposit.

Based on "ROXI" WG outcomes, the ST3 of RI-URBANS on PM speciation provides detailed guidance for QA/QC, data treatment and reporting data/uncertainties of Xact. To ensure a good quality of measurement, checks and maintenance operations as well as data control and validation should carefully follow the recommendations provided in section 3.2.3. Moreover, the user must refer to the dedicated manuals from the instrument manufacturers listed in section 3.2.1.

This document will be followed by a well-developed SOP and harmonized source apportionment recommendations based on the existing online trace element datasets collected across Europe.

#### 5.1.3. **Data management**

According to EU legislation, the member states are obliged to submit the data to the European Air Quality Portal (EAQP) run by the European Environmental Agency (EEA). However, some guidance

on how to do the data management locally within the AQMNs is needed, and will be provided by EEA. Also, it is needed to clarify what will be the situation for the measurements at supersites within the NAQD? Do the member states need to send the data to EAQP from the EEA as it is the case for other air pollutants? Probably the later will be the AQ option. If this is the case, it is recommended to the EAQP to follow the data management and templates from EBAS protocols. The EAQP will have to develop protocols and templates for submitting the data on PM components. For the moment these requirements refer to daily data. Here, we included also advanced measurements with hourly resolution.

Here we report on the guidance for data management protocols implemented by ACTRIS in EBAS for these advanced measurements, in some cases able to collect data in hourly resolution, in addition to the daily ones.

The usual data flow within ACTRIS consists of annual data submission to the EBAS-NILU database (EBAS-NILU, <https://ebas.nilu.no/delivery/>). The EBAS protocols were established by EBAS in collaboration with EMEP and ACTRIS infrastructures.

Most datasets on PM speciation collected under RI-URBANS are not openly available via the EBAS data depository. An effort on data homogenisation and sharing in open format would be beneficial to a better AQ policy support.

For ACSM data, a comprehensive tool has been developed called ACMCC\_Export (Jean-Eudes Petit, at CEA/LSCE), suitable both for Q-ACSM and ToF-ACSM.

There is currently no specific protocol for submitting Xact data to European archive databases such as EBAS. The recent integration of ROXI user group to ACTRIS as a dedicated working group might initiate the future development of an export tool for releasing PM elemental concentrations and uncertainties to EBAS in the requested format.

## 5.2. Main observations regarding PM speciation at urban European sites

### 5.2.1. Offline PM speciation

- **Limited number of sites, and mostly from Southern Europe:** There is a lack of PM chemical composition data in central and northern Europe. This hampers the study of the spatial and temporal variability of PM levels, composition, and sources across Europe. Only a few monitoring sites from Southern Europe were included in this review, potentially affecting the

comprehensiveness of the results for this region.

- **There are reference methods for most major PM components** that shall be followed when speciating PM samples.
- **Lack of harmonisation of measurements of trace elements other than As, Cd, Ni, and Pb:** There is a significant lack of harmonisation for most trace elements in measurement techniques and data reporting among the different countries and sites, which could influence the comparability and consistency of the data.
- **Data availability:** Not all datasets are openly accessible, posing challenges for further independent analysis and validation by the wider scientific community.
- **Trace elements:**
  - The most abundant trace elements in PM<sub>10</sub> were Zn, Ti and Cu.
  - The average concentrations of As, Pb, Cd, and Ni complied with EU air quality standards of 6, 500, 5, and 20 ng m<sup>-3</sup>, respectively.
  - Carcinogenic Cr and Ni accounted for 3% and 2%, respectively, of the total trace element mass concentrations.

### 5.2.2. Online PM speciation

#### *Instrument and data management*

- The number of sites in Europe measuring NR-PM<sub>1</sub> online using ACSM and AMS is low. We compiled data from 35 sites (26 UB, 5 SU, 3 TR, and 1 RB). 28/35 datasets contained more than one year of data since several datasets of shorter campaigns were included, especially those making use of the AMS instrumentation.
- Not all sites provided comparisons to collocated measurements, implying that the QA/QC procedures are not guaranteed for all sites.
- Not all the presented datasets are openly available. An effort on data homogenisation and sharing in open format would be beneficial to a better AQ policy support.

#### *Concentrations of NR-PM<sub>1</sub>*

- Mean NR-PM<sub>1</sub> concentration in Europe for the compiled datasets is  $10.7 \pm 6.9 \mu\text{g m}^{-3}$ . NR-PM<sub>1</sub> is very spatially heterogeneous. The dataset with highest concentrations was that from Granada, an urban background site with an average NR-PM<sub>1</sub> concentration of 36  $\mu\text{g/m}^3$ .
- NR-PM<sub>1</sub> mass concentration does not clearly depend on the types of site, except for the fact that regional background sites present the lowest concentrations. The concentrations at urban,

suburban or traffic sites are not homogeneous and seem to be much sensitive to site specific meteorological conditions and emission patterns.

- OA is generally the major component of NR-PM1. Southern sites, especially those near the Mediterranean coast, present larger sulphate concentrations.
- Depending on the inorganic relative composition of the NR-PM1 compounds, three groups of sites can be differentiated: i) nitrate driven, typically with high traffic influence; ii) sulphate-driven, generally characterised by sea and/or shipping influence; iii) intermediate sites between i and ii; iv) high chloride concentrations in Krakow, likely related to coal burning.
- Seasonal variability of NR-PM1 and its compounds depends on the above classification. Nitrate-driven sites are more prone to highly-polluted winter episodes whilst summer concentrations generally are higher at sulphate-driven sites.
- Diel cycles differ depending on the types of sites. OA, nitrate, and ammonium concentrations follow the traffic cycles, especially for the traffic and urban sites, whilst no clear diel variation is observed at RB sites. Nitrate and chloride concentrations present a homogeneous pronounced minimum at all types of sites in the central hours of the day due to volatilisation at higher temperatures.

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