A European aerosol phenomenology - 7: high-time resolution chemical characteristics of submicron particulate matter across Europe

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ABSTRACT

Similarities and differences in the submicron atmospheric aerosol chemical composition are analyzed from a unique set of measurements performed at 21 sites across Europe for at least one year. These sites are located between 35 and 62°N and 10° W – 26°E, and represent various types of settings (remote, coastal, rural, industrial, urban). Measurements were all carried out on-line with a 30-min time resolution using mass spectroscopy based instruments known as Aerosol Chemical Speciation Monitors (ACSM) and Aerosol Mass Spectrometers (AMS) and

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following common measurement guidelines. Data regarding organics, sulfate, nitrate and ammonium concentrations, as well as the sum of them called non-refractory submicron aerosol mass concentration ([NR-PM_1]) are discussed. NR-PM_1 concentrations generally increase from remote to urban sites. They are mostly larger in the mid-latitude band than in southern and northern Europe. On average, organics account for the major part (36–64%) of NR-PM_1 followed by sulfate (12–44%) and nitrate (6–35%). The annual mean chemical composition of NR-PM_1 at rural (or regional background) sites and urban background sites are very similar. Considering rural and regional background sites only, nitrate contribution is higher and sulfate contribution is lower in mid-latitude Europe compared to northern and southern Europe. Large seasonal variations in concentrations (μg/m^3) of one or more components of NR-PM_1 can be observed at all sites, as well as in the chemical composition of NR-PM_1 (%) at most sites. Significant diel cycles in the contribution to [NR-PM_1] of organics, sulfate, and nitrate can be observed at a majority of sites both in winter and summer. Early morning minima in organics in concomitance with maxima in nitrate are common features at regional and urban background sites. Daily variations are much smaller at a number of coastal and rural sites. Looking at NR-PM_1 chemical composition as a function of NR-PM_1 mass concentration reveals that although organics account for the major fraction of NR-PM_1 at all concentration levels at most sites, nitrate contribution generally increases with NR-PM_1 mass concentration and predominates when NR-PM_1 mass concentrations exceed 40 μg/m^3 at half of the sites.

1. Introduction

In the European Union (EU), Particulate Matter (PM) is regarded by the European Environment Agency as the air pollutant most harmful to human health (EEA, 2019). For 2017, more than 370 000 premature deaths were attributed to long-term exposure to $PM_{2.5}$ (PM with aerodynamic diameter below 2.5 μm) in the EU-28 (EEA, 2019), corresponding to ca. 3.8 million years of life lost (3 days/inhabitant). Recently, the link between short-term exposure to PM and daily mortality has also been confirmed by the evaluation of data from over 600 cities across the world, of which more than 100 in Europe (Liu et al., 2019). PM has not only respiratory and cardiovascular adverse effects (WHO, 2006, 2013). It has also been classified as carcinogenic to humans by the International Agency for Research on Cancer since 2013 (Loomis et al., 2013). As a step towards WHO guidelines, various EU directives have attempted to reduce PM impacts on human health - and the environment - during the last decades by setting daily limit values for PM_{10}, annual limit values for PM_{10} and $PM_{2.5}$, long term exposure reduction targets for $PM_{2.5}$, as well as emission ceilings for aerosol precursors (e.g. EU, 1996, 1999, 2008, 2016). As a consequence, PM concentrations have generally decreased at most types of site in Europe over the last 20 years (Tørseth et al., 2012; EEA, 2019). However, the rate of decrease in total European population exposure to $PM_{2.5}$ seems to be rather slow (-0.5 μg m^{-3} yr^{-1}) over the last decade (EEA, 2019). Thus, there is a need to further reduce PM levels and impacts in Europe, which requires a better knowledge of its physical and chemical properties. PM is indeed a complex mixture of components including organic matter, inorganic salts, elemental carbon, trace metals, etc. A better understanding of PM chemical composition in Europe is necessary to identify its sources (e.g. Zhang et al., 2011), assess its toxicity (Kelly and Fussell, 2012), estimate its impacts on climate (Boucher et al., 2013), improve air quality models (Kukkonen et al., 2012) and support air quality related policies (Heal et al., 2012; EC, 2013).

Very few peer-reviewed publications have described the overall chemical composition of particulate matter based on long-term in-situ measurements across Europe (Putaud et al., 2004, 2010; Tørseth et al., 2012). These studies analyzed data from the EMEP (European Monitoring and Evaluation Programme) data base (ebas.nilu.no) to show that European PM chemical composition strongly depends on the PM size fraction, the geographical location within Europe, the type of site, and the time period. These works highlighted the need to reduce the uncertainties associated with the difference in the techniques used to collect and analyze PM samples, mainly affecting the data regarding semi-volatile and carbonaceous particulate species, respectively. They did not specifically address the submicron fraction of the aerosol (PM_1), which contains particles of anthropogenic origin that contribute importantly to PM toxic effects (Vu et al., 2018), can travel far away from sources, and play a major role in climate change (Raes et al., 2000). Previous works did not either deal with the short-term variations in PM concentration and composition. In contrast, Crippa et al. (2014) used high-time-reslolution data in their study focused on submicron organic aerosol characteristics at 17 sites across Europe, but these data had been obtained from 3 series of 15–50 day long measurements campaigns.

Our study is based on long (>1 year) time series of half-hourly mean concentrations of major constituents of the non-refractory fraction of PM_1 (NR-PM1). These data were produced under the European Aerosols, Clouds, and Trace gases Research InfraStructure (ACTRIS, www.actris.eu). To provide long-term, high-quality and comparable aerosol chemistry data, Aerosol Chemical Speciation Monitors (ACSM, Aerodyne Inc.) have been implemented at more than 20 ACTRIS observatories across Europe, starting from 2011 (www.psi.ch/acsm-stations/overview-full-period). The ACSM is based on a similar technology as the Aerosol Mass Spectrometer (AMS, Aerodyne Inc.; Canagaratna et al., 2007), and provides high-time resolved (30 min) information on the chemical composition (organics, nitrate, sulfate, ammonium and chloride) of non-refractory submicron PM (Ng et al., 2011; Fröhlich et al., 2013) and more recently also NR-$PM_{2.5}$ (Xu et al., 2017; Zhang et al., 2019). This technology is not prone to the sampling artefacts which affect the collection of semi-volatile PM components by filters (e.g. Viana et al., 2006; Kim et al., 2015). It is suitable for long-term (months to years) stable operation at various types of site, from urban to remote observatories (e.g. Canonaco et al., 2015; Fröhlich et al., 2015a; Minguillón et al., 2015; Parworth et al., 2015; Sun et al., 2018; Zhang et al., 2019). ACSM measurements are part of the revised EMEP monitoring program for 2020–2029 (UN-ECE, 2019).

Based on the compilation and statistical analysis of long-term in-situ measurements performed with ACSM and AMS instruments, this work makes use of the specificities of on-line measurements to highlight similarities and differences in the chemical composition of the non-refractory submicron aerosol across Europe on various scales. Like previous "European aerosol phenomenology" articles (e.g. Putaud et al., 2010), it merely describes general features observed in the sets of data available at the time of the study. Implications for further developments of PM abatement policies are discussed in light of these results.

2. Material and methods

2.1. Sampling sites

The measurements performed at 21 selected sampling sites located in 13 different countries across Europe (Fig. 1) were processed. A detailed description of each sampling site - including coordinates, altitude, data coverage, related networks, etc.- can be found in Table S1 (Supplement). Fifteen sites contribute to at least one of the existing international programs for air pollution measurements, such as the World Meteorological Organization - Global Atmosphere Watch network (gaw.empa.ch/

gawsis), the United Nations' Convention on Long Range Transboundary Air pollution – European Monitoring and Evaluation Programme (www.emep.int) and the European Union's ACTRIS research infrastructure (www.actris.eu), whereas six sites are operated in other contexts.

These 21 sampling sites have been classified following the recommendations of the European Environment Agency (Larssen et al., 1999), as in the previous phenomenology studies (e.g. Putaud et al., 2010). According to their distance from large pollution sources, the 21 sites considered in this study (Table S1) are: one natural background (or remote) site (more than 50 km distant from large pollution sources), eleven rural or regional background sites (10–50 km distant from large pollution sources), five urban background sites representative of the "average air pollution levels in urban areas", one industrial site defined as "typically hot-spot stations located in areas with sharp gradients", and three coastal sites (an additional category introduced for rural background sites located less than 2 km downwind from the sea shore). Site classification has always been questionable, and some of our 21 sites have been classified differently in previous works (e.g. Ripoll et al., 2014; 2015; Petit et al., 2015).

The 21 sites have also been classified in three geographical regions according to their latitude: northern Europe (NE) for the five sites north of 53°N, mid-latitude Europe (ME) for the eleven sites located between 45°N and 52°N, and southern Europe (SE) for the 5 sites located south of 43°N. These three geographical regions were chosen to highlight intra-regional similarities and inter-regional differences in the submicron aerosol properties. Other possible geographical sectorizations would have certainly led to other interesting results.

2.2. Instrumentation

The chemical composition of non-refractory submicron aerosols (NR-PM_1) was determined by a Quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM, Ng et al., 2011) at 18 sites, a Time-of-Flight ACSM (ToF-ACSM, Fröhlich et al., 2013) at 1 site, and a compact ToF Aerosol Mass Spectrometer (cToF-AMS, Drewnick et al., 2005) at 2 sites during the years 2011–2015. All these instruments (Table S1) were developed by Aerodyne Research Inc. For each of them, the operating principle is similar to the one described by e.g. Jayne et al. (2000), Drewnick et al. (2005), Canagaratna et al. (2007), Fröhlich et al. (2013), and Ng et al. (2011). Briefly, for all instruments, sampled aerosol particles are focused by an aerodynamic lens, travel through vacuum chambers, and are vaporized after impacting a resistively heated porous tungsten surface (~600 °C). Molecular fragments are ionized by Electron Ionization (70 eV), and subsequently detected by a mass spectrometer. The mass spectrometer is either a quadrupole analyzer (residual gas analyzer type) for the Q-ACSM (Ng et al., 2011), or a Tofwerk time-of-flight analyzer for the ToF-ACSM and the cTof-AMS (Drewnick et al., 2005). The mass spectra detected by the mass spectrometers are then converted to mass concentrations of NR-PM_1 major chemical species - namely organics, sulfate, nitrate, ammonium and chloride -, following the methodology described in e.g. Allan et al. (2004), Canagaratna et al. (2007) and references therein, and Jimenez et al. (2003).

The ACSM particle collection efficiencies are better than 50% and 90% for the aerodynamic diameter ranges 75–650 nm, and 120–320 nm respectively (Liu et al., 2007). For the AMS, these ranges enhance to 60–1000 nm and 100–600 nm, respectively. Better mass resolutions and

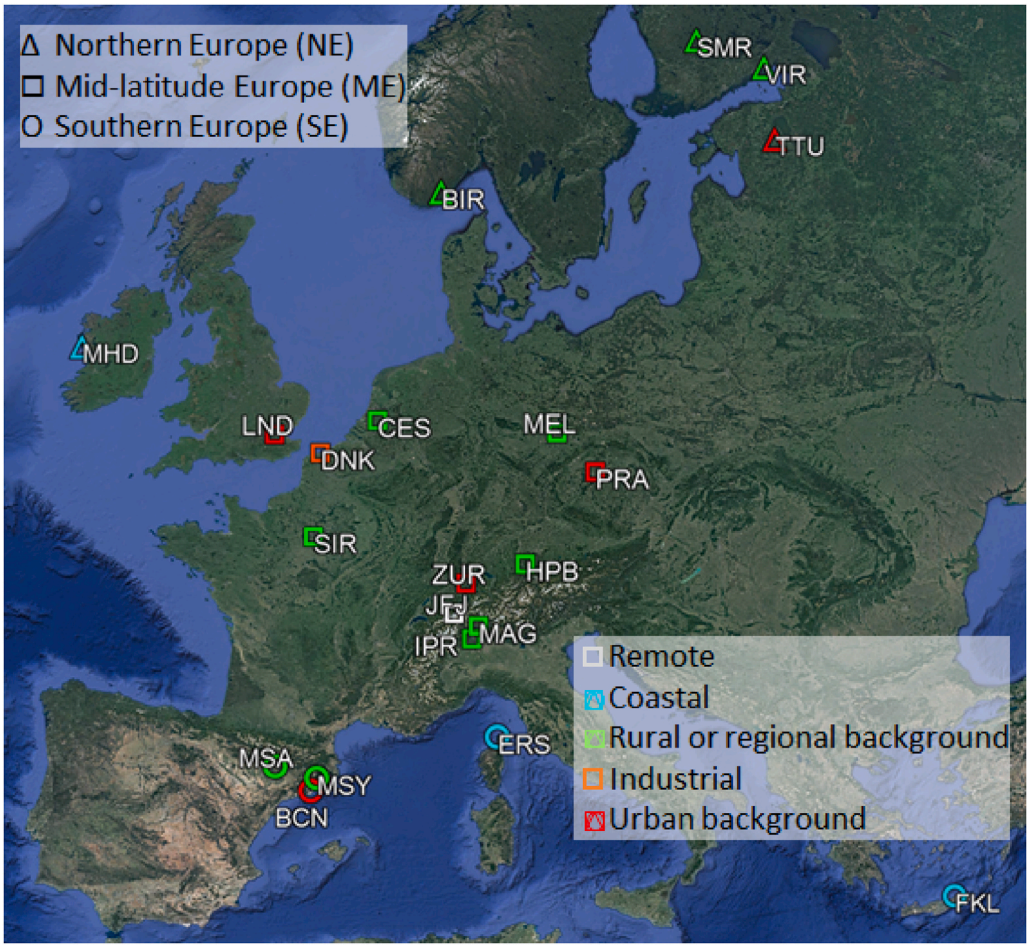

Fig. 1. Sampling site locations, distinguished by type and geographical regions (see Table S1 in Supplement for further details). Map designed with Google Earth 7. February 3, 5776 (Google Inc.).

detection limits are also achieved in the latter case (Fröhlich et al., 2013).

Q-ACSMs were operated following the recommendations given in ACTRIS-ACSM guidelines (2015), Aerodyne (2011a, 2011b) and Ng et al. (2011). In particular, all Q-ACSM users followed the recommendations for setup, calibration, operation, maintenance and data analysis described at that time in the "ACTRIS-ACSM best practice document" (www.psi.ch/acsm-stations/acsm-best-practice). This document has been edited by the European ACTRIS-ACSM community to help operate Q-ACSMs in a proper and consistent manner with the aim of ensuring the comparability of the various ACSM datasets produced across Europe. A more detailed description of the ACSM and AMS operating procedures followed at each site can be found in the Supplement (Section 1), where the determination of the collection efficiency (CE), the ionization efficiency for nitrate (IE), and the relative ionization efficiency (RIE) for ammonium and sulfate are described and tabulated (Table S3). Relevant publications providing further details are also listed.

Sixteen instruments participated in inter-comparisons (Table S4) at the time of the measurements described here. Among them, eleven Q-ACSMs and the ToF-ACSM participated in the same 3-week inter-instrument comparison in 2013 at the Aerosol Chemical Monitor Calibration Center (ACMCC, acmcc.lsce.ipsl.fr/doku.php), which is part of the European Centre for Aerosol Calibration (www.actris-ecac.eu). The reproducibility expanded uncertainties of this set of Q-ACSMs were estimated to 9, 15, 19, 28 and 36% for NR-PM_1, nitrate, organics, sulfate and ammonium, respectively (Crenn et al., 2015). Three Q-ACSMs delivered unsatisfactory data for chloride, probably partly due to potential issues related to the use of the default fragmentation table (Tobler et al., 2020), and to the very low chloride concentrations experienced during that workshop. Chloride data are therefore not considered for the remainder of this work. The ToF-ACSM generally showed good agreement with the median of the 11 Q-ACSMs for NR-PM_1 mass and major chemical species ($R^2 \geq 0.8$, $0.8 < slope < 0.9$), ammonium excepted (Crenn et al., 2015). The Q-ACSM operated in Dunkirk was satisfactorily compared to a HR-ToF-AMS for 10 days in 2014 and with independent on-line measurements (Zhang et al., 2021). The cToF-AMS used in London (UK) was compared with a co-located High Resolution-ToF-AMS (DeCarlo et al., 2006), and also showed good agreement ($R^2 > 0.9$, $0.9 < slope < 1.3$) for major NR-PM_1 species (Young et al., 2015). Uncertainties and discrepancies across instruments should still be borne in mind when comparing the data obtained at the various sites of this study.

At all sites, ACSM and AMS data were compared to data obtained independently by at least one other instrument (Supplement, Table S3). Particle Mobility Spectrometers, Optical Particle Counters or Tapered Element Oscillating Microbalances were used to evaluate NR-PM_1 mass concentration ([NR-PM_1]) data, while PM component concentrations obtained from off-line or on-line thermal-optical analysis and ion chromatography were used to check the measurements of organics and ionic species, respectively. Comparisons between the sum of NR-PM_1 chemical component determined by ACSM or AMS (corrected for elemental or equivalent black carbon when relevant and possible) and PM mass concentrations derived from independent measurements show a fair agreement ($0.65 < R^2 < 0.98$, $0.73 < slopes < 1.21$) at the 19 sites where PM_1 could be estimated. This indicates a good consistency despite fundamental differences amongst these various techniques, including their lower and upper cut-off diameters (see Supplement and Table S3). Fewer sites reported comparisons for organics (10), sulfate (14), nitrate (12) or ammonium (9). Fair agreements ($0.76 < R^2 < 0.97$) were found where sulfate and nitrate in PM_1 were measured. The slopes of the regressions are better distributed around one for sulfate ($0.63 < slope < 1.19$) than for nitrate ($1.23 < slope < 2.80$), most certainly due to filter sampling negative artefacts affecting ammonium nitrate collection (Schaap et al., 2004). Fairly good correlations ($0.69 < R^2 < 0.92$) between organics measured by ACSM or AMS and organic carbon (OC) determined independently were also observed (see Supplement and Table S3).

It should be noted that only nitrate IE and the ammonium RIE could be properly determined by the time these measurements were performed. Sulfate RIE were mostly assessed empirically (see Supplement Section 1), whereas a default RIE value of 1.4 was recommended for organics in ambient air. New calibration procedures allow for a more accurate determination of sulfate RIE as well as for investigating possible overestimation of the m/z 44 organic-related fragment (Fröhlich et al., 2015b; Pieber et al., 2016; Freney et al., 2019). Such calibration procedures were not available by the time of the measurements analyzed in this study, but no *a posteriori* correction of the datasets obtained several years earlier could be envisaged.

2.3. Data processing

Datasets from the 21 selected sites were gathered by the Joint Research Centre, after correction for CE, IE, and RIE performed by each data originator to produce as accurate as possible data from their instrument (see Supplement Section1 for details). Fifteen of the ACSM datasets used in this study are currently available from the openly accessible EBAS database (ebas.nilu.no) operated by the Norwegian Institute for Air Research (NILU). The other datasets are available on request from the authors of the present work.

The temporal coverage of the selected ACSM and AMS datasets was uneven, with the first measurement starting in February 2011 and the last one ending in May 2015 (Fig. S2). Three assumptions were made to permit comparisons among sites. First, a dataset was assumed to be representative of a given season (Spring: MAM, Summer: JJA, etc.) if data covered more than 45 days during this season (i.e. data coverage higher than ~50%). This criterion of 50% data coverage is low compared to the minimum data capture of 90% for particulate matter reported in the data quality objectives of the European directive 2008/50/EC, but it is still high compared to the large majority of ACSM or AMS based studies, which are typically conducted during ca. 10–30 days in a given season (Jimenez et al., 2009; Ng et al., 2010; Crippa et al., 2014). Second, a dataset was assumed to be representative of a full year of measurements if comprising at least three seasons, including summer and winter. All 21 datasets selected for this study are representative for the 4 seasons and a full year of measurements. Seasonal averages were calculated from all the data available for each season, and annual statistics from entire years to avoid over representing one or several seasons with respect to others. Third, PM inter-annual variability was assumed to be negligible across the 4-year period of measurements (2011–2015). This assumption could possibly have two limitations due to inter-annual climate variability (Andersson et al., 2007; Barmpadimos et al., 2012), and long-term decreasing PM trend at some European sites (e.g. Tørseth et al., 2012; Querol et al., 2014; Zhang et al., 2019). Nevertheless, based on chemical transport model simulations of $PM_{2.5}$ concentrations from 1958 to 2001 over Europe, Andersson et al. (2007) estimate that the average European $PM_{2.5}$ concentrations inter-annual variability due to meteorology is 7% only. In addition, the European Environment Agency reports a mean decrease in $PM_{2.5}$ levels at all sites of -0.48 ± 0.11 μg/m^3 per year (EEA, 2019) over 2011–2015, while a previous report showed that trends were very small at urban and rural background sites over the 2006–2012 time period (EEA, 2014). Since our study is based on measurements made mainly at rural or regional and urban background sites, it can reasonably be assumed that the inter-annual variations in NR-PM_1 were quite little over the 4-year period 2011–2015. However, we observed that component's average contributions (%) are more robust (e.g. less sensitive to the period selected to calculate annual statistics) than mass concentrations (μg/m^3).

3. Results and discussion

Standardized and quality controlled measurements of NR-PM_1

components performed with the same analytical technique at 21 European sites for periods long enough to be representative for a full year are reported here together for the first time. Several of these measurements have already been discussed in site specific publications (see Supplement Table S3). We focus here on similarities and differences across these 21 sites on the European scale rather than on site peculiarities.

3.1. Annual averages

3.1.1. Mass concentrations

The lowest annual mean NR-PM_1 concentration (0.8 μg/m^3) was observed at Jungfraujoch (CH), our remote mountain site. Annual average NR-PM_1 concentrations ranged from 2.8 to 14 μg/m^3 across the other sites (Fig. 2), reflecting the diversity of the European environments we considered. Comparable NR-PM_1 levels have been reported in Northern America (1.4–19 μg/m^3 across 12 sites) by Jimenez et al. (2009), whereas the extreme concentrations measured in South America, e.g. 41 μg/m^3 in Mexico City, Mexico (Salcedo et al., 2006) or in Asia, e.g. 63 μg/m^3 in Beijing, China (Huang et al., 2010), and 87 μg/m^3 in Delhi, India (Gani et al., 2019) were not observed at our set of sites in Europe (Fig. S3). This possibly results from efficient air quality policies implemented in Europe (Hey, 2005; Tørseth et al., 2012; Fuzzi et al., 2015) and North America (US EPA, 2011, 2019) during the last decades. There are currently neither limit values nor target values for PM_1 pollution levels to compare these data with. Nonetheless, annual NR-PM_1 mean concentrations measured at 4 sites of our study – Tartu (EE), Zurich (CH), Prague (CZ) and Ispra (IT) – were higher than the WHO guidelines of 10 μg/m^3 for $PM_{2.5}$ (WHO, 2006) and close to that value (9<[NR-PM_1]<10 μg/m^3) at 4 others– Dunkirk (FR), Magadino (CH), London (UK) and Melpitz (DE) –, including several regional background sites. Since the relationship between exposure to fine PM and health response is linear and without any threshold below which fine PM does not affect human health (WHO, 2013), reducing NR-PM_1 levels would anyway be beneficial everywhere.

The type and geographical location of the 21 sites are indicated in Fig. 2 to help understand NR-PM_1 inter-site variability. A gradient from remote to coastal to rural and regional background to urban background locations (annual grand averages = 0.8, 4.5, 7.7 and 10.6. μg/m^3, respectively) is generally observed (as highlighted in Fig. 2b), underlying the influence of local sources on NR-PM_1 concentrations. Several exceptions can be noticed, with specific rural or regional background sites like Ispra (IT) or Hyytiälä (FI) exhibiting NR-PM_1 levels comparable to urban or coastal locations, respectively. The type of site is hence not sufficient to fully explain the submicron aerosol concentration variability across Europe. Their geographical location within Europe must also be taken into account. Considering sites' latitude in Fig. 2b reveals that NR-PM_1 concentrations are generally higher in ME compared to SE and NE (see also Table 1). The assessment of NR-PM_1 mass concentration data quality indicates that such differences cannot be due to biases in aerosol mass spectrometers' measurements. High NR-PM_1 levels observed at rural or regional background locations in ME (grand average = 9.1 μg/m^3) compared to SE and NE (6.2 and 4.3 μg/m^3, respectively) suggest a homogeneous and elevated submicron aerosol background level in mid-latitude Europe. Larger emission rates of fine particles and precursors in ME is probably the main cause. Other possible reasons including variations in meteorological conditions that could have produced variations in pollution advection, aerosol wet removal rates, and/or photochemical production of secondary organic and inorganic aerosol, could also explain the higher NR-PM_1 levels observed in SE compared to NE. Differences in the collection efficiency of the instruments operated in NE (possible slight low bias) and SE (possible slight low bias) also cannot be excluded. Eventually, a possible slight impact of interannual variations in NR-PM1 concentrations cannot be rigorously ruled out.

3.1.2. Chemical composition

Since air pollutant concentrations are largely affected by vertical and horizontal dispersion and therefore very variable, the variations in organics, sulfate, nitrate and ammonium across our 21 sites are discussed in terms of contributions to the sum ([NR-PM_1]) of all the components measured by the AMS or ACSM. These variables are of course different from the contributions of these species to PM_1 since the refractory components of PM_1 are not taken into account. They are however independent from pollution dilution rates, but obviously not independent from each other.

Large annual average contributions of organic aerosol (range 36–64%, grand average 51%) are observed at all sites (Fig. 3a). Sulfate is on average the second most important component of NR-PM_1 (grand average 21%, range 12–44%). Its contribution equals or exceeds that of organic aerosol only at Mace Head (IE) and Finokalia (GR), both coastal sites. Nitrate (grand average 15%, range 6–35%) becomes the second highest contributor to NR-PM_1 after organics and on par with sulfate at

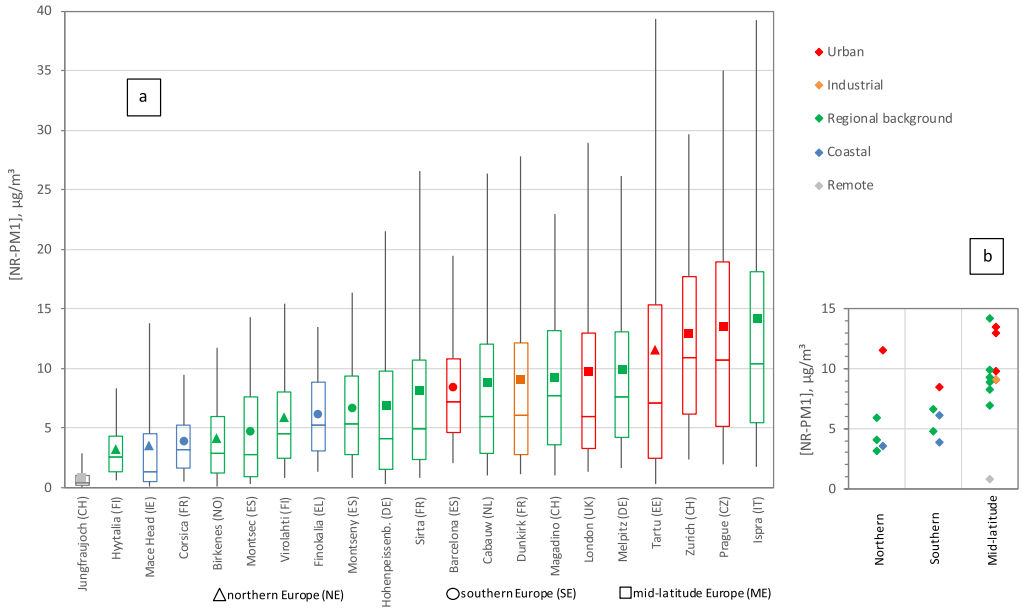

Fig. 2. Annual NR-PM_1 concentrations across Europe. Panel (a): Box plots constructed from the 5th, 25th, 50th, 75th and 95th percentiles; averages indicated by the symbol in box (Δ = northern, = mid-latitude, O = southern Europe). Colors indicate the type of site (see legend). Panel (b) shows again the annual averages classified according to the 3 latitude zones (see Section 2.1). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Annual NR-PM_1 mass concentrations (μg/m^3) and chemical composition (%) statistics at the various types of site across Europe and at regional background sites in northern, southern and mid-latitude Europe.

		Type of site					Regional background		
		Remote	Coastal	Rural & Regional background	Industrial	Urban background	Northern Europe	Southern Europe	Mid-latitude Europe
	Nr of sites	1	3	11	1	5	3	2	6
[$NR\text{-}PM_1$] (μg. m^{-3})	av	0.8	4.5	7.7	9.1	10.6	4.3	6.2	9.1
	std	1.0	4.2	8.3	9.2	10.1	4.0	5.5	9.3
	med	0.4	3.3	5.0	6.0	7.3	3.0	4.8	6.2
	25th-75th	0.2–1.0	1.4–6.2	2.3–10.3	2.8–12.1	3.7–14.2	1.5–5.8	2.1–8.9	2.8–12.3
Organics (%)	av	49	44	54	38	50	60	55	53
	std	18	15	17	18	18	18	13	17
	med	49	44	55	37	50	60	55	54
	25th-75th	37–62	34–54	42–68	24–51	37–63	47–74	46–64	40–67
Sulfate (%)	av	27	34	16	28	19	22	20	14
	std	16	13	10	20	11	13	10	9
	med	23	34	14	22	17	20	19	13
	25th-75th	15–36	25–43	9–22	13–39	11–25	12–29	13–26	8–19
Nitrate (%)	av	8	8	18	21	18	8	12	22
	std	7	7	14	14	14	8	10	14
	med	7	6	13	18	14	5	9	18
	25th-75th	4–12	4–9	6–27	9–30	7–26	3–9	5–18	9–32
Ammonium (%)	av	16	14	11	13	13	11	13	11
	std	12	7	7	5	6	9	5	6
	med	12	13	11	13	13	9	13	11
	25th-75th	8–20	10–17	7–15	10–17	9–16	5–14	10–16	7–15

av: average, std: standard deviation, med: median, 25th - 75th: 25th percentile and 75th percentile.

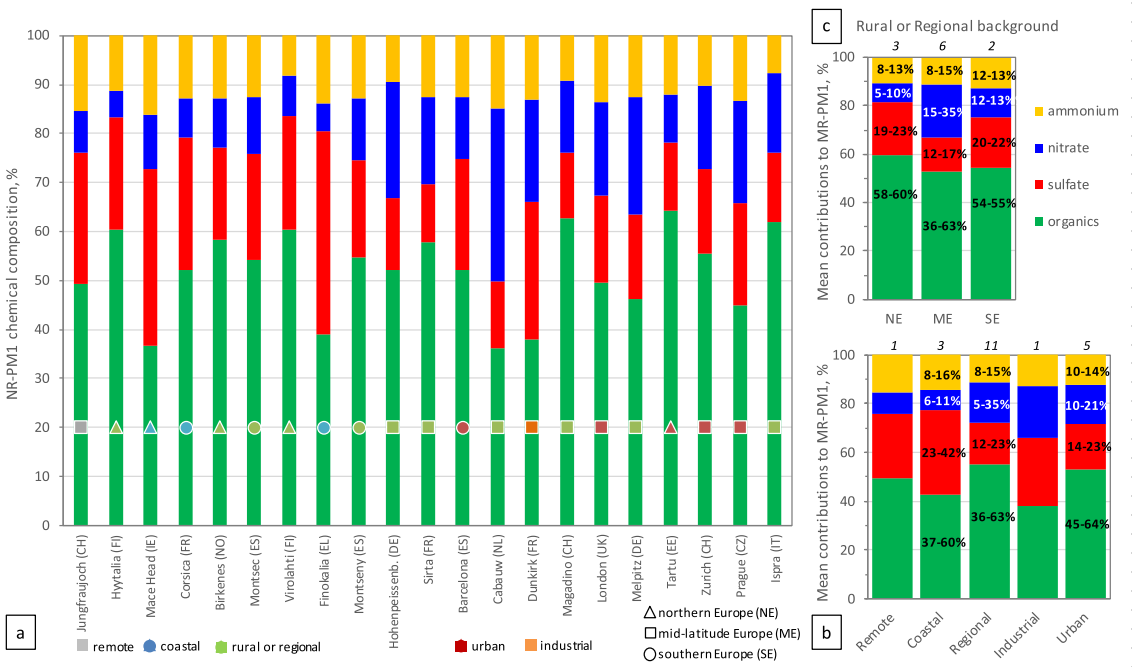

Fig. 3. Annual average NR-PM_1 relative chemical composition across Europe. Symbols in panel (a) indicate the type of site and the latitudinal location. In panels (b) and (c), percentages (%) are the ranges of the annual averages and figures in italics are the number of sites for each category.

Magadino (CH), London (UK), Zurich (CH), Prague (CZ) and Ispra (IT), and significantly ahead of sulfate at Hohenpeissenberg (DE), Sirta (FR), Cabauw (NL), and Melpitz (DE), i.e. all the regional and urban background sites located in ME. Interestingly, notable nitrate contributions (10–28%) are observed at five locations in summer (Prague, Melpitz, Hohenpeissenberg, Dunkirk (FR), Cabauw). Nitrate contributions would have most probably been largely underestimated by classical filter-based measurements that are prone to negative sampling artefacts for semi-volatile species at ambient temperatures >20 °C (see e.g. Schaap et al., 2004; Kulkarni et al., 2011). Nitrate is the only species for which the annual mean contribution to NR-PM_1 significantly (99% confidence level) correlates with the annual mean NR-PM_1 across our 21 sites (see

Section 3.4). Ammonium concentrations are closely related to those of sulfate and nitrate, as a consequence of sulfuric and nitric acid neutralization by ammonia (see Table S2). However, we observed that sulfate and nitrate are not always fully balanced by ammonium at Jungfraujoch, Hyytiälä, Mace Head, Virolahti, Finokalia, Hohenpeissenberg, Cabauw, Dunkirk, London, Zurich and Ispra. This may be due to NH_3 shortages at e.g. remote or coastal sites, or to significant concentrations of organic nitrates at NO_x-rich locations. Indeed, recent high resolution measurements showed that a significant part of the nitrate consists of organic nitrates at various sites across Europe (Kiendler-Scharr et al., 2016). Ammonium contributes on average for 12% (range 8–17%) to [NR-PM_1].

NR-PM_1 grand average chemical composition at coastal sites is rather similar to the one at the remote site of Jungfraujoch (CH), and the grand average chemical compositions at regional and urban background sites look very similar to each other (Fig. 3b). However, the limited number of sites of each type, and the variability of the chemical composition among sites of the same type reduce the statistical significance of these observations. Nevertheless, the predominance and similarity of organics' contribution at all types of site are strongly suggested by our data set. This could be explained by i) the wide variety of primary and secondary organic aerosol sources, ranging from local - e.g. food cooking in urban areas (Mohr et al., 2012; Minguillón et al., 2016), and domestic wood burning (Crippa et al., 2014) - to natural sources - e.g. marine biogenic at coastal locations (Karl et al., 2015) and primary and secondary biogenic aerosol in forested areas (Yttri et al., 2011; Minguillon et al., 2016) - which could compensate each other, ii) the co-emission of organic and inorganic particulate compounds or precursors from major sources (e.g. combustion processes), iii) physico-chemical processes affecting similarly both organic and the inorganic species (e.g. condensation in winter and photochemical production in summer) and iv) the relatively long lifetime of submicron particles resulting in relatively small gradients in their chemical composition from source regions to regional background regions when averaged over a full year (Donahue et al., 2013).

In contrast with organics, annual mean nitrate contributions vary largely across Europe (6–35%; Fig. 3a). Remarkable differences can be noticed between remote + coastal and urban + regional background sites (8 and 18%, respectively, Fig. 3b). Local anthropogenic emissions of nitrogen oxides (NO_x) - mostly from road and non-road transport, energy transformation and industrial combustion in Europe (Pay et al., 2012) - therefore play a key role in particulate nitrate formation. Urban and regional background sites exhibit very similar annual mean nitrate contributions (18%), which could be explained by compensation effects. Indeed, ammonium nitrate is essentially a secondary pollutant coming from the reaction between nitric acid (formed by the atmospheric oxidation of NO_x) and ammonia. The formation of particulate ammonium nitrate can be ammonia or nitric acid sensitive in HNO3- and NH3-rich air, respectively, depending also on the aerosol pH and water content (Petetin et al., 2016; Nenes et al., 2020).

As for nitrate, sulfate contributions to NR-PM_1 largely differ across Europe (12–44%) depending on site type and location. On average, higher contributions are found at remote and coastal areas (~30%) compared to regional and urban locations (below 20%). Data quality assessments give confidence that this difference cannot be due to instrumental biases (see Table S3). At coastal sites, sulfate concentrations are not significantly less than at some of the regional and even urban background sites, although major sulfur dioxide (SO_2) sources are located in the vicinity of the latter both. However, SO_2 emissions have sharply decreased in Europe during the last 30 years (Smith et al., 2011; Chin et al., 2014) thanks to the implementation of specific measures, e.g. the European NEC Directive (EU, 2016) and the United Nation Gothenburg (1999) protocol on sulfur emissions. The highest sulfate contributions reported in coastal areas can then be related to: i) shipping emissions of SO_2 (Viana et al., 2014), ii) marine phytoplankton emissions of dimethylsulfide (Quinn and Bates, 2011) influencing coastal sites, iii) the slow conversion (3–4 days) of SO_2 to sulfate in the gas phase and the liquid phase (cloud droplets) possibly hundreds of km away from SO_2 sources (Stein and Lamb, 2002 and references therein) and iv) low conentrations of organics and nitrates due to low concentrations of gaseous precursors (volatile organic compounds and NOx) in the marine atmosphere.

Comparing regional backgrounds in northern, mid-latitude, and southern Europe, statistically significant (99% confidence level) differences in NR-PM_1 grand mean chemical composition can be highlighted. The contribution of nitrate is greater at ME sites compared to NE and SE sites, due to generally much higher concentrations of nitrate in ME. In contrast, the contribution of sulfate is less in ME than in NE and SE, partly due to moderate sulfate concentrations in ME, but mainly because of higher nitrate and organics concentrations in the mid-latitude band (Fig. 4). Comparisons with independent measurements of nitrate and sulfate indicate that such differences cannot be attributed to inaccuracies in aerosol mass spectrometer measurements (see Table S3). The fact that there is no significant difference in nitrate contribution between northern and southern Europe suggests that the different NR-PM_1 chemical composition observed in ME compared to other latitudes comes more from differences in the emission of particulate nitrate and sulfate precursors (including ammonia) than from differences in atmospheric processes (volatilization and/or condensation of ammonium nitrate and photochemical production of sulfate). There is no significant difference in contributions of organics across the 3 latitudinal zones (NE, ME and SE) although all NE sites (SMR, BIR, VIR) exhibit annual relative contributions of organics larger than 55%, likely due to the combination of the little anthropogenic influence (leading to low levels of ammonium, nitrate and sulfate), and also to substantial concentrations of organic aerosol from spring to summer (Fig. 4), coming from biogenic aerosol sources (Daellenbach et al., 2017).

3.2. Seasonal variations

Seasonal statistics in NR-PM_1 mass concentrations are shown in Fig. 4. While low particulate pollution periods ([NR-PM_1] < 5 μg/m^3) can be observed at any site during any season, acute particulate pollution events ([NR-PM_1] > 30 μg/m^3) are only exceptionally observed during summer. All sites where [NR-PM_1] is least in summer (Sirta, FR; Barcelona, ES; Dunkirk, FR; Tartu, EE, Zurich, EE; Prague, CZ) are urban or industrial sites, except Sirta (FR), which is however located only 20 km SW of Paris city center. These minima are mainly due to lower nitrate concentrations, even if organics' concentrations are also lower in summer compared to other seasons at most of these sites. In contrast, the NR-PM_1 seasonal maxima observed in summer at Jungfraujoch (CH), Hyytiälä (FI), Corsica (FR), Montsec (ES), Finokalia (GR), and Montseny (ES) are all due to increased concentrations in organics and sulfate, except in Hyytiälä (organics only). All these sites are little polluted, and three out of five sit in southern Europe. Large increases of sulfate concentrations in summer are also observed in Barcelona (ES), Hohenpeissenberg (DE), London (UK), and Ispra (IT). High summertime sulfate concentrations may be attributed to a faster photochemical production of sulfate.

The seasonal variations in NR-PM_1 chemical composition (Fig. 4) are much less than the seasonal variations in NR-PM_1 concentrations. For instance, seasonal mean chemical compositions are almost identical at the two rural sites in Finland, while concentrations are about twice as high in Virolahti (FI) compared to Hyytiälä (FI). Similarly, the NR-PM_1 chemical compositions are almost constant across the 4 seasons at Corsica (FR) and Finokalia (GR) while concentrations vary by a factor of more than 2 at both Mediterranean coastal sites. Seasonal variation magnitudes (maximum/minimum ratio) in components' contributions to NR-PM_1 are greatest for nitrate (range 1.4–4.6), and smallest for organics and ammonium (range 1.1–1.7 for both). Large seasonal variations in nitrate contribution (with minima in summer everywhere but Jungfraujoch, CH) likely result from an increased volatilization of NH_4NO_3 during warmer periods, while the more constant contribution

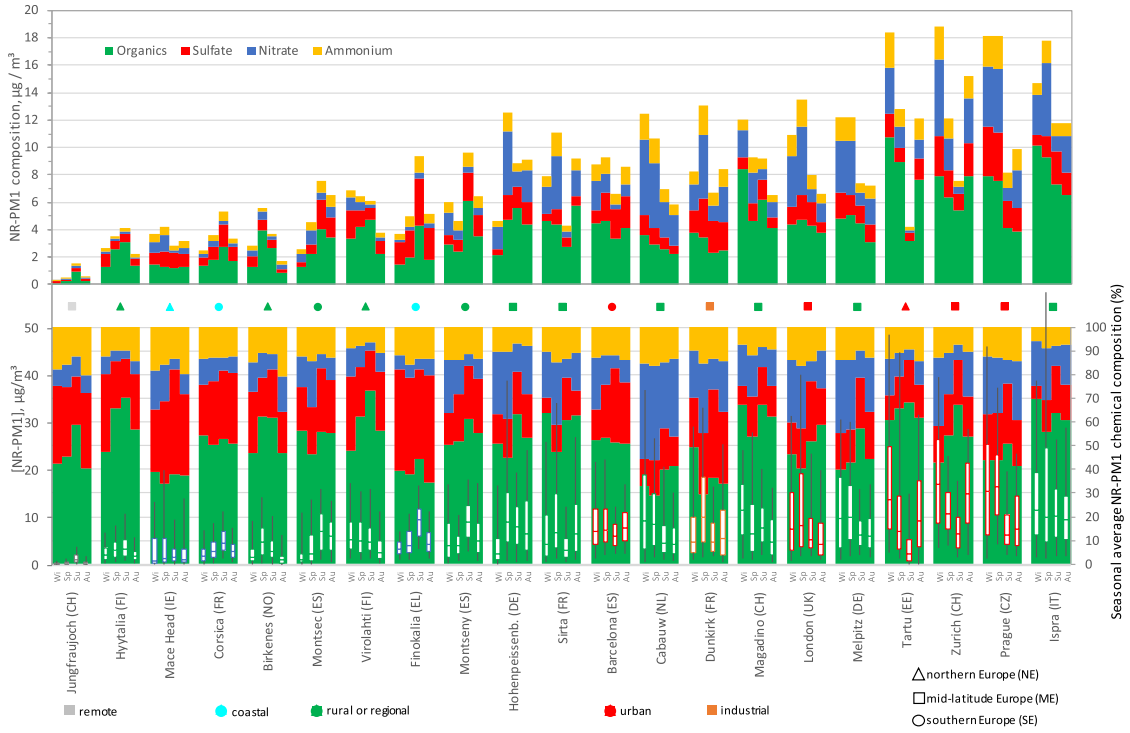

Fig. 4. Seasonal statistics in NR-PM_1. Top panel: average concentrations of organics, sulfate, nitrate, and ammonium. Bottom panel: box plots constructed from the 5th, 25th, 50th, 75th and 95th percentiles of NR-PM_1 mass concentrations (left hand y-axis), and average chemical composition (right hand y-axis). Symbols between the 2 charts indicate sites type and location (see legend).

of ammonium could come from the production of $(NH_4)_2SO_4$ counter-balancing the volatilization of NH_4NO_3 during summer. The fairly constant contribution of organics across the year could be at least partly explained by the large variety of organic aerosol sources with opposite seasonal cycles like wood burning for domestic heating (higher during colder months) vs. formation of secondary biogenic aerosols (higher during warmer months). The seasonal variations in NR-PM_1 chemical composition still greatly differ across the 21 sites of our study, suggesting that various factors influence NR-PM_1 with different weights during the 4 seasons at most sites. The coastal sites in the Mediterranean emerge as exceptions with fairly constant NR-PM_1 chemical compositions across the year.

3.3. Diel cycles

Hourly median contributions of organics, sulfate and nitrate (Fig. 5) were calculated for winter (DJF) and summer (JJA) months separately. The time used to plot these diel variations is the official local time in winter, and local time −1 in summer. Diel cycles are highlighted by fitting 24-hr periodic sinusoidal functions to the hourly median values when reasonable (average residual < 20%). Diel cycle patterns can be roughly classified in three main categories: 1) fairly constant contributions of organics, sulfate and nitrate over 24 h, 2) minimum contribution of organics (often corresponding with maximum contribution of nitrate) before sunrise and 3) other diel patterns, including minimum in organics' and maximum in nitrate contribution during daylight period. Diel variations in sulfate are generally not much marked, and too diverse to be used as a classification criterion. Possible explanations to these three patterns are discussed below. The daily cycles in concentrations ($\mu g/m^3$) presented in the Supplement (Fig. S4) can also help understand the daily cycles in NR-PM_1 chemical composition discussed below.

3.3.1. "Flat" diel cycles

The magnitude of the diel cycles (defined as daily maximum – daily minimum) in the contribution of organics, sulfate and nitrate is at most 8% for both winter and summer in Birkenes (NO), Corsica (FR), Hohenpeissenberg (DE), Hyytiälä (FI), Mace Head (IE), and Virolahti (FI), and for winter only in Finokalia (GR) as shown in Fig. 5a and b (left hand column). These sites are all clean mountain, coastal or rural sites, which are mostly impacted by long range transported aged aerosol. The diel variations in organics and nitrate are clearly not affected by volatilization/condensation cycles in winter, and at most slightly only in summer. The greatest diel variations are observed for sulfate at Finokalia (GR) and Mace Head (IE) in winter (maximum sulfate contribution before sunrise), and at Hyytiälä and Virolahti (FI) in summer (maximum sulfate contribution after noon). The latter could be explained by an increased photo-chemical production of sulfate in the afternoon during summer.

3.3.2. Minimum in organics contribution at night (before sunrise)

Clear minima in the contribution of organics are observed at night (generally just before sunrise) for both winter and summer months in Cabauw (NL), London (UK), Montseny (ES), Sirta (FR), Prague (CZ), Tartu (EE), and Zurich (CH). Such minima in the contribution of organics before sunrise are also observed in winter only in Barcelona (ES), Ispra (IT), and Melpitz (DE), and in summer only in Montsec (ES) and Jungfraujoch (CH) as shown in Fig. 5a and b (middle column). For Montsec and Jungfraujoch, the increase in the contribution of organics during daytime in summer could be explained by the strong growth of the mixed boundary layer during the warmest hours of the day (Ripoll et al., 2015; Fröhlich et al., 2015), bringing carbon enriched aerosol up to the sampling sites. A comparable increase is observed for nitrate contribution in Jungfraujoch, but not in Montsec where this effect is probably counter-balanced by NH_4NO_3 volatilization due to higher temperatures. All other sites with minimum contribution of organics at night (Cabauw, NL; London, UK; Montseny, ES; Sirta, FR; Prague, CZ; Tartu, EE; Zurich, CH; Barcelona, ES; Ispra, IT; and Melpitz, DE) are urban sites or regional background sites located in the vicinity of

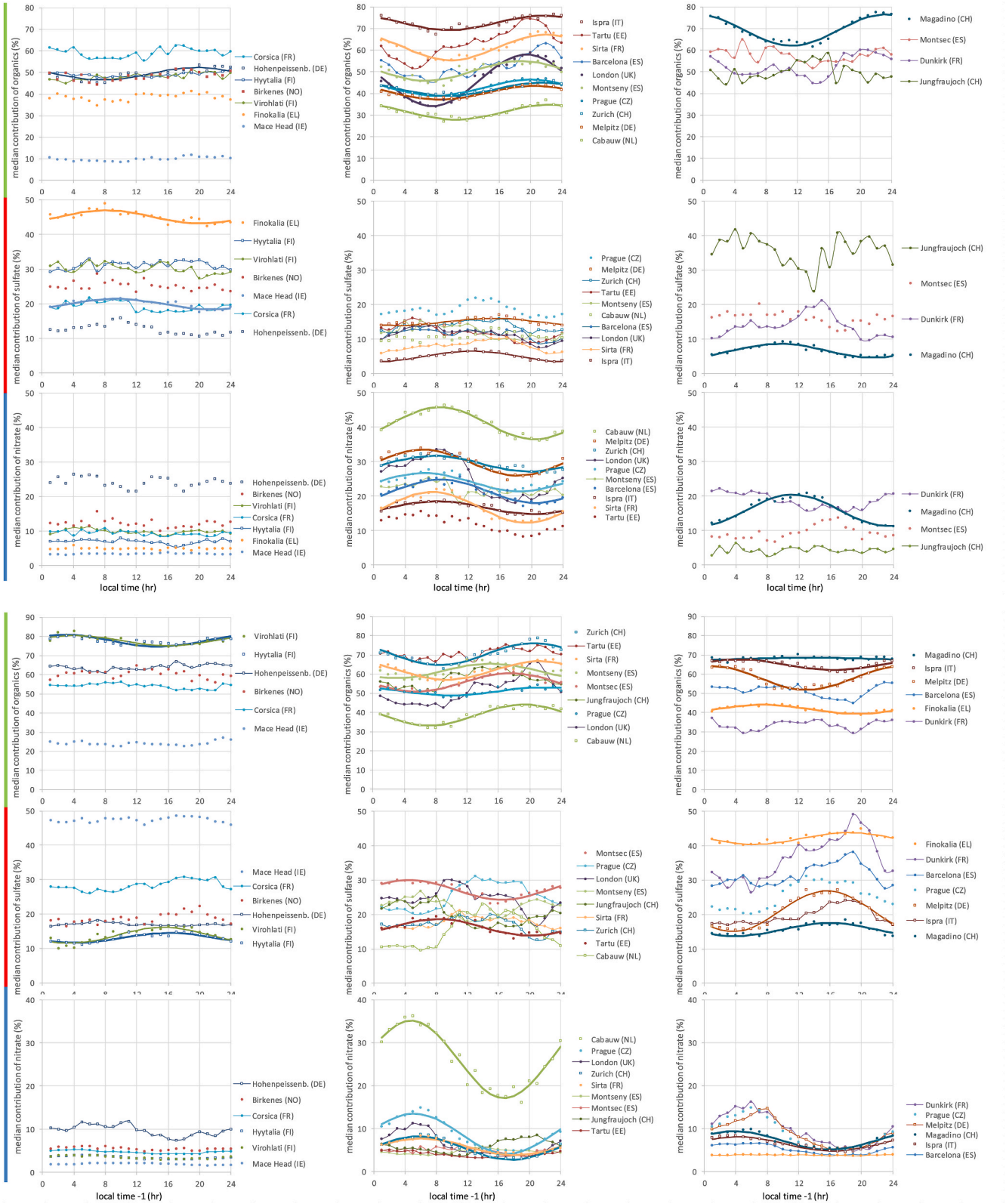

Fig. 5. a: Winter mean daily cycles in organics (top), sulfate (middle) and nitrate (bottom) contributions to NR-PM_1. Sites are roughly classified according to the shape of the daily cycles in organics and nitrate. Sinusoidal functions (thick lines) were fit to the data points when appropriate
Fig. 5b: Same as Fig. 5a for summer.

conurbations from where particulate air pollution can be transported within a few hours. However, nitrate contribution maxima before sunrise and minima after noon (i.e. with a 12-hr phase shift compared to organics) can also be observed at all these sites (except Tartu in summer). Possible explanations for these observations include increased emissions from wood burning in the evening in winter, and enhanced

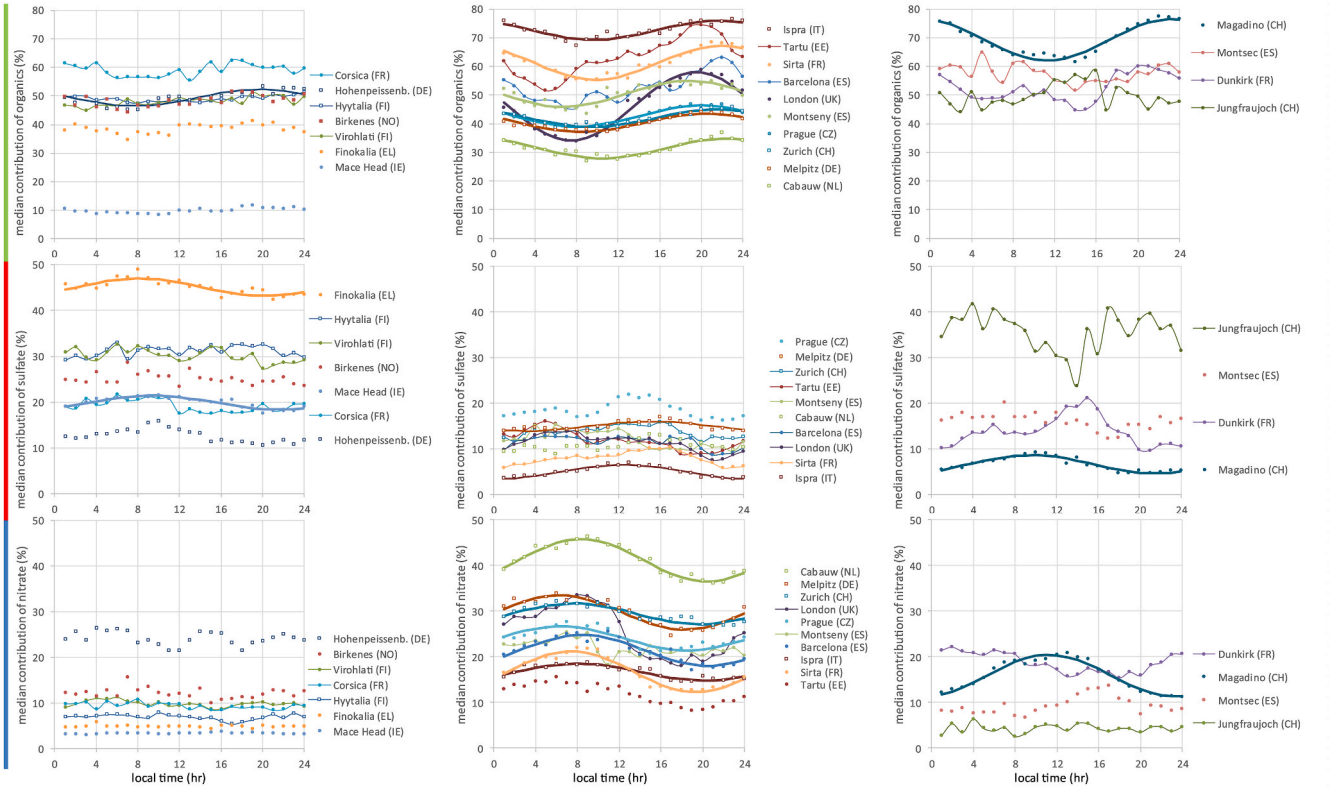

Fig. 5. (*continued*).

production of secondary organic aerosol in the afternoon in summer. The partial volatilization of particulate nitrate during daytime can also directly contribute to the afternoon minima in nitrate and indirectly participate in the afternoon maxima in organics' contribution to NR-PM_1.

The hourly median contribution of sulfate is rather constant over 24 h (variation magnitude at most 7%) in winter at all these sites. In contrast, it is quite variable (variation magnitude up to 13%) in summer at some sites including Cabauw (NL), London (UK), and Prague (CZ), where sulfate concentrations up to double during day time compared to night time. The most straightforward explanation for this would be the greater photochemical production of sulfate during day time in summer. However, the maximum contribution of sulfate also can be observed during night at other sites (e.g. Montsec, ES; Tartu, EE), mainly due to the fact that sulfate concentrations do not drop down at night as concentrations of organics (the main NR-PM_1 component) do.

3.3.3. Other diel patterns

Jungfraujoch (CH) is the only site with a maximum contribution of organics during daytime in winter (Fig. 5a, right hand column). This maximum coincides with a minimum contribution of sulfate, while the contribution of nitrate remains quite constant over the day. Significant diel variations are difficult to explain at such a mountain site, which mostly sits in the free troposphere in winter and can be affected by low altitude air masses only in particular meteorological situations (strong southerly Foehn winds or passing of cold fronts).

In contrast, the contribution of organics is minimum during daytime in winter at a few other sites (Dunkirk, FR; Magadino, CH), concomitant with a maximum in nitrate contribution in Magadino (CH). Such diel cycles are consistent with evening increased emissions of organic aerosol from domestic wood burning in winter (Vlachou et al., 2018).

In summer (Fig. 5b, right hand column), the minimum in organics contribution also occurs between noon and late afternoon in Barcelona (ES), Finokalia (GR), Ispra (IT), and Melpitz (DE). The minimum in nitrate contribution is also observed in the afternoon at 3 of these sites, Finokalia being the exception with a very flat diel cycle. Low contributions of organics and nitrate during the hottest hours of the day point to the volatilization of semi-volatile particulate nitrate and organics as a driver of the observed diel cycles. The afternoon peak in sulfate contribution observed at these 3 sites - and also at Dunkirk (FR), Magadino (CH) and Prague (CZ) - could also result from an increased photochemical production of sulfate from about noon in summer (See Supplement, Fig. S4).

3.4. Chemical composition of NR-PM_1 as a function of [NR-PM_1] levels

3.4.1. Observations

Fig. 6 shows the variations in NR-PM_1 chemical composition as a function of NR-PM_1 mass concentrations with a 1 $\mu g/m^3$ resolution in NR-PM_1 for each site. Averages were calculated excluding measurements where the contribution of one or more component(s) was negative. Results are shown for [NR-PM_1] bins in which at least ten 30 min-long measurements were available to ensure a reasonable representativeness of all data points.

Relatively constant chemical compositions, irrespective of NR-PM_1 mass concentrations, are observed at only a couple of sites (Fig. 6) like Finokalia (GR) and Jungfraujoch (CH), which are mainly impacted by long-range transport of air pollution.

At most sites, the composition of NR-PM_1 indeed varies with [NR-PM1] (Fig. 6). Although organics remain the main component of NR-PM_1 at any concentration level at 12 of the 21 sites of our study, organics contribution actually decreases while the contribution of nitrate increases with NR-PM_1 mass concentration at most (13) of the sites. This pattern is primarily observed in ME (9 from 13 sites), and at all urban sites. This could be explained by conditions (low temperatures, shallow mixed boundary layer, long nights) favoring both the accumulation of particulate matter and the formation of particulate ammonium and organic nitrates. The percentage of wintertime measurements

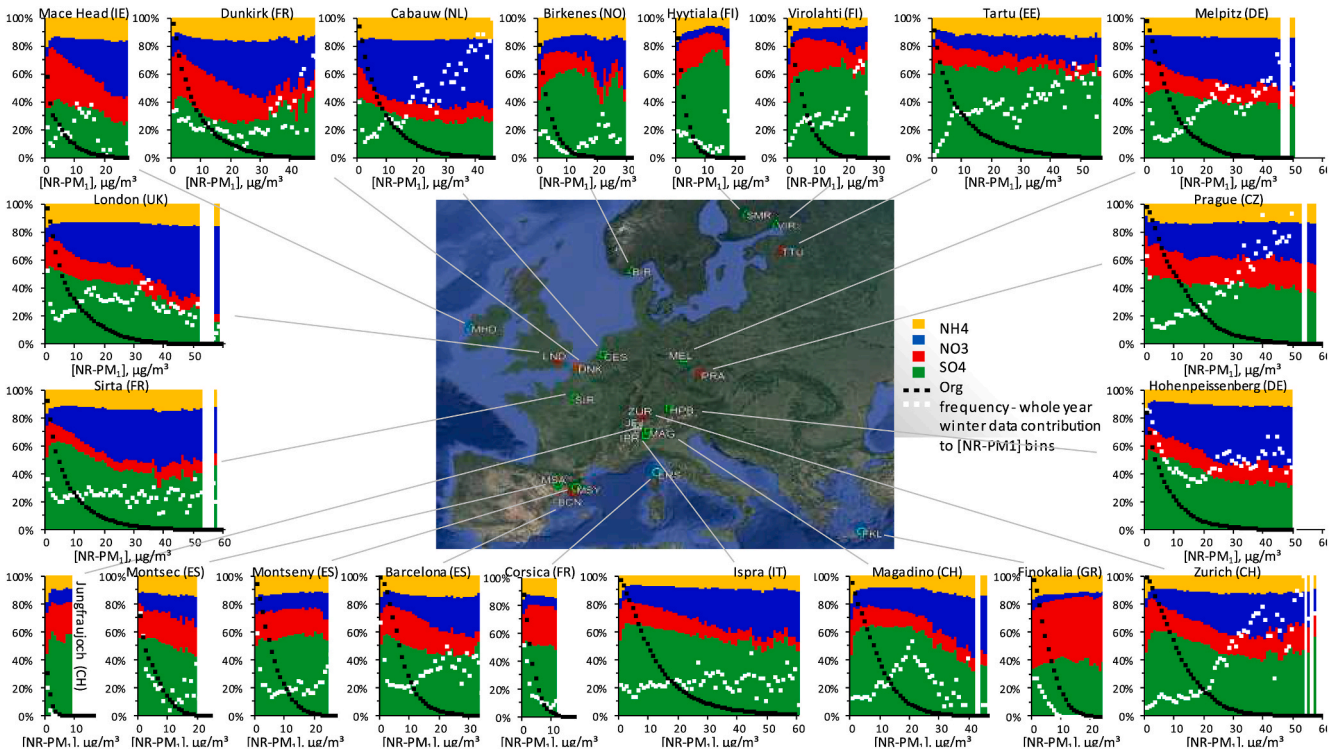

Fig. 6. Relative chemical composition (%) as a function of NR-PM_1 mass (annual coverage). Black dots indicate the frequency of occurrence of NR-PM_1 concentrations greater than the value on the x-axis (cumulative frequency of occurrence). White dots indicate the percentage of wintertime data contributing to each mass bin. Map designed with Google Earth 7.February 1, 2041 (Google Inc.).

contributing to each NR-PM1 mass bin is also shown in Fig. 6. High [NR-PM_1] levels (and corresponding nitrate-rich chemical compositions) mainly reflect winter conditions in e.g. Cabauw (NL), Melpitz (DE), Zurich (CH) as expected, but not in e.g. Sirta (FR), London (UK) and Ispra (IT). Low temperatures associated with large [NR-PM_1] levels and large nitrate contributions may certainly also occur during seasons other than winter. However, other phenomena like peaks in NO_x emissions or specific pollution advection pathways can as well lead to increases of both NR-PM_1 mass concentrations and nitrate contributions.

Eight sites show other patterns (Fig. 6). An increasing contribution of organics is for instance observed for NR-PM_1 mass concentration increasing up to 15 µg/m^3 (e.g. Hyytiälä, FI; Birkenes, NO) or from 20 µg/m^3 at a few sites (e.g. Dunkirk, FR). Quite specifically, the contribution of sulfate increases with NR-PM_1 concentrations at Finokalia (GR) only.

If high PM_1 concentrations were resulting only from the accumulation of particulate matter due to unfavorable meteorological conditions (e.g. shallow mixed boundary layer, lack of precipitation, weak winds), its chemical composition would *a priori* remain independent from its concentration. Our data confirm that other factors also contribute to the occurrence of high NR-PM_1 levels, possibly including variations in specific source intensities, changes in pollution advection pathways, and increases in condensation rates of semi-volatile species. The latter can arise from lower temperatures (e.g., at night or during winter) and/or greater numbers of adsorption sites resulting from particle accumulation primarily due to weather conditions.

3.4.2. *Implications for PM abatement policies*

At 12 out of 21 sites, annual or daily mean [NR-PM_1] exceeding the WHO annual or daily guideline values for $PM_{2.5}$ were observed. Different suggestions for PM abatement policies can be formulated depending on the objectives sought. On average (Sect. 3.1.2), organics dominate NR-PM_1 chemical composition at most European locations, which suggests that measures focused on the mitigation of organic aerosol would be efficient to comply with the European annual limit and target values for PM concentrations or similar regulations. The apportionment of organic aerosol into oxygenated and hydrocarbon-like organics was performed at 9 sites only (Table S4), which does not allow us to describe further the sources of organic aerosol across the various site types or latitudinal zones previously defined. However, specific studies performed at several sites of this study showed that most of the submicron organic aerosol is secondary (i.e. formed from gaseous organic compounds via atmospheric reactions), and that most of it is from non-fossil origin (Minguillón et al., 2011, 2015, 2016; Canonaco et al., 2013; Fröhlich et al., 2015a; Ripoll et al., 2015; Bressi et al., 2016; Vlachou et al., 2018; Zhang et al., 2019). Its non-fossil origin may indicate biogenic sources and biomass burning as important aerosol sources of organic carbon in summer and winter, respectively (Canonaco et al., 2015). However, at five of the studied sites (all in ME), nitrate becomes the major component of NR-PM_1 for mass concentrations greater than 40 µg/m^3. This suggests that focusing on nitrate abatement would be particularly efficient at tackling acute particulate pollution episodes and reducing the risk of exceeding PM daily limit values at that type of site. Potentially both NO_x and ammonia emission reductions could smooth down sharp particulate pollution peaks dominated by ammonium nitrate.

No single strategy will be sufficient to fulfil the requirements of air quality directives regarding both daily and annual limit values in PM concentrations. Coping with the air quality legislation should nevertheless not be an end in itself. It is rather a mean "to achieve levels of air quality that do not give rise to significant negative impacts on, and risks to, human health and the environment" (EU, 2013). If we focus on the impacts of PM on human health, both short-term and long-term exposures should be considered, since they "contribute to different stages of disease development within an individual or population subgroups at certain points in time" (WHO, 2013). From this temporal perspective, both particulate organics and nitrate should be targeted in Europe. The adverse health impact of individual chemical components could possibly

also be considered at some point. Particulate sulfate and nitrate compounds were reported not to cause excess health risks in past toxicological studies (Schlesinger and Cassee, 2003; Reiss et al., 2007; WHO, 2013). In contrast, there is growing evidence on the associations of carbonaceous matter with health effects (Zanobetti et al., 2009; Delfino et al., 2010; WHO, 2013). However, the role of PM major components in PM adverse health effects has not been definitively elucidated yet (US EPA, 2019). It is therefore too early to envisage the development of legislative rules addressing separately organics, sulfate, nitrate and ammonium for the scope of protecting human health. In contrast, chemical speciation of PM shall systematically be performed in support to epidemiological studies in the future. This will provide the information needed to further develop the air quality related legislation, possibly addressing specific PM components or sources.

4. Conclusions and perspectives

Non-refractory submicron aerosol mass concentration and chemical composition measured on the long-term at high temporal resolution using the same standardized analytical technique at 21 sites across Europe (Fig. 1) are presented. These 21 sites were classified according to their type (remote, coastal, rural or regional background, urban and industrial) and geographical location (northern, southern and mid-latitude Europe). The following conclusions can be drawn:

1 Annual average NR-PM_1 mass concentrations ranged from 2.8 to 14 $\mu g/m^3$ across all sites except the remote mountain site (0.8 $\mu g/m^3$). NR-PM_1 mass generally presents an increasing gradient from coastal to regional background to urban background sites, and from northern to southern to mid-latitude Europe at regional background sites (Fig. 2). In particular, a quite homogeneous and elevated submicron aerosol background level is observed in mid-latitude Europe.
2 The three major chemical constituents of NR-PM_1 are in order organics, sulfate and nitrate. (Fig. 3). Organics' contribution is substantial at all sites (annual averages = 36–65%). The variability in the contribution of organics is large within each class of type or latitude band, and no significant difference across these categories can be highlighted. Sulfate and nitrate present a wider range of annual mean contributions (12–44% and 5–35%, respectively). The grand average chemical compositions of NR-PM_1 at regional and urban background sites do not significantly differ from each other. In contrast, nitrate contribution is on average greater and sulfate contribution is on average lower at mid-latitude compared to northern and southern Europe regional background sites (Table 1). This is due to higher concentrations of nitrate in mid-latitude Europe, but also to substantial concentrations of sulfate in northern and southern Europe (Fig. 4). Latitudinal gradients can be better explained by differences in nitrate and sulfate precursor emissions than by atmospheric processes.
3 The seasonal variations in NR-PM_1 chemical composition are much less than the variations in NR-PM_1 components' concentrations (Fig. 4). Nitrate shows the largest seasonal variations with minima in summer (except at the remote mountain site), which can be explained by a greater volatilization rate of NH_4NO_3 during warmer months.
4 The main constituents of NR-PM_1 show marked daily cycles at most sites both in winter and summer (Fig. 5). The most commonly observed diel variations are characterized by maxima in organic aerosol contribution in the afternoon or in the evening, generally concomitant with minima in nitrate contributions. Such diel variations are observed at remote to urban sites, and from southern to northern Europe. The diel cycles in sulfate are generally less pronounced, but at the few sites where they are significant, maxima in sulfate contribution occur during the afternoon. The daily cycles in NR-PM_1 chemical composition can be explained by diel changes in the emission of particulate matter and precursors, which can be amplified by atmospheric processes. No significant diel variations in NR-PM_1 chemical composition could be detected at a few sites only. Those include only coastal and rural sites (mostly in southern and northern Europe), where long range transport of aged aerosol predominates.
5 NR-PM_1 chemical composition generally varies with NR-PM_1 mass concentration (Fig. 6). Organics remain the major component of NR-PM_1 at all concentration levels at most sites, but nitrate contribution commonly increases with NR-PM_1 mass (13 sites), especially in mid-latitude Europe (10 sites). Large contributions of nitrate associated with high levels of NR-PM_1 do not exclusively occur in winter and can probably not be related to low air temperatures only.
6 Suggestions for smart PM abatement policies on the European scale depend on the objectives sought (e.g. legislative vs. human health impacts, annual vs. daily limit values, long-term vs. short-term exposure, …). Organic aerosol shall certainly be tackled as the main NR-PM_1 component on the annual average at most of the European sites we studied, but nitrate shows up as a major species at high NR-PM_1 mass concentration levels at most sites.

CRediT authorship contribution statement

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Declaration of competing interest

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

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Appendix A. Supplementary data

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