Intercomparison of online and offline XRF spectrometers for determining the PM_{10} elemental composition of ambient aerosol

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Keywords: X-ray fluorescence analysis; XRF intercomparison, on-line spectrometry, PM_{10}

Abstract

Measuring the elemental composition of atmospheric particulate matter (PM) can provide useful information on the adverse effects of PM and help the identification of emission sources. Carrying out these measurements at a high time resolution (1-h or less) allows to describe the fast processes to which aerosol particles are subjected in the atmosphere, leading to a better characterisation of the emissions. Energy dispersive X-ray fluorescence spectrometry (ED-XRF) is one of the most widespread techniques used to determine the elemental composition of PM. In recent years, new systems known as online XRF spectrometers have been developed to provide real-time measurements of the PM elemental concentration at a high time resolution. Among these advanced instruments, the Xact® 625i Ambient Metals Monitor by Cooper Environmental (USA) performs in situ automated measurements with a user selected time resolution ranging from 15 to 240 min. In this study, an Xact® 625i monitor equipped with a PM_{10} inlet was deployed for nearly 6 months (July-December 2023) in Milan (Po Valley, Italy) at a monitoring station of the Lombardy Regional Agency for Environmental Protection (ARPA Lombardia). The instrument was configured to quantify 36 elements, ranging from Al to Bi, with 1-h time resolution in the PM_{10} fraction. The objective of the study was to verify the correct functioning of the instrument and to evaluate the quality and robustness of the data produced. Xact® 625i data were aggregated to 24-h daily means and then compared to 24-h PM_{10} filter data retrieved by ARPA Lombardia in the same station and analyzed offline for the elemental concentration with a benchtop ED-XRF spectrometer. The intercomparison focused on the 16 elements (Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb) whose concentrations were consistently above their minimum detection limits (MDL) for both online and offline techniques. Results of the intercomparison were satisfying showing that the Xact® 625i elemental

concentrations were found to be highly correlated to the offline ED-XRF analyses (R^2 ranging from 0.67 to 0.99) and slopes ranging from 0.79 to 1.3 (just a couple of elements showed slopes up to 1.70).

1. Introduction

Measurement and quantification of the chemical composition of atmospheric particulate matter (PM) are key aspects of air quality monitoring. It has long been known that PM is associated with adverse impacts, which are influenced by the chemical composition of the particles. At the global scale, PM affects cloud formation and Earth's radiative budget (Fuzzi et al., 2015); at the local scale, its harmfulness on human health is of particular concern (Brunekreef and Holgate, 2002; Kelly et al., 2012; Rohr and Wyzga, 2012; Daellenbach et al., 2020). Therefore, it is important to achieve a more detailed knowledge about which chemical components are responsible for these negative effects. Determining the composition of PM is also a fundamental step to perform source apportionment studies for the identification of the emission sources, which help the implementation of mitigation strategies (WHO, 2013).

Trace elements, in particular metals, although they generally do not contribute substantially to the mass of PM are of interest because they act as tracers for specific sources (Visser et al., 2015) and some of them are associated to adverse health effects even at ambient level concentrations (Chen and Lippmann, 2009). The quantification of these elements in PM samples can be obtained through various techniques (see e.g., Ogrizek et al., 2022), among the most widespread there are e.g., energy dispersive X-ray fluorescence spectrometry (ED-XRF), particle-induced X-ray emission (PIXE), and wet-chemistry inductively coupled plasma mass spectrometry (ICP-MS). All these methods require the collection of aerosol particles on filters, followed by laboratory analysis. ED-XRF is a non-destructive technique and does not require any sample pre-treatment (e.g., repeated analyses on the same sample and quantification of different chemical components in the same sample are possible), detects simultaneously multiple elements (20-30) with Z>10 using an X-ray tube for irradiating the samples, and it is typically operated using benchtop instruments. For decades until today, it has been largely applied to aerosol analysis in research laboratories as well as in monitoring networks like e.g., the U.S. Environmental Protection Agency Chemical Speciation Network (https://www.epa.gov/amtic/chemical-speciation-network-csn-general-information). One advantage of ED-XRF is that it is quite stable and does not require frequent calibrations so that it is suitable for automated spectrometer development.

PIXE analysis uses accelerated particles (often protons with energies of a few MeV) as irradiation source and it has been traditionally used to assess the elemental composition in aerosol filter samples (see e.g., Lucarelli et al., 2020; and therein cited literature). Although being more sensitive than ED-

XRF, PIXE has some features in common with ED-XRF such as the capability of providing quantitative information for elements with Z>10 (being both based on fluorescence X-rays detection), the unnecessary sample pre-treatment and the non-destructive character. While the need of an accelerator facility makes the beam-time availability for PIXE analysis a shortcoming, the existence of very effective PIXE set-up where a high number of filter samples can be robustly and effectively analyzed in short times helps a lot in large monitoring campaigns with many samples to be characterized. As an example, at the INFN-LABEC facility in Florence, Italy, the typical irradiation time for each daily aerosol sample is 45-60 s depending on the mass loading (vs. approximately 1-h per sample with ED-XRF) and, more interestingly, also 1-h resolution samples can be analyzed in 1 min per spot (see e.g., Calzolai et al., 2010, 2015; Lucarelli et al., 2011).

ICP-MS is a very sensitive and fast analytical technique for detecting trace and ultra-trace elements (>50 elements simultaneously) in aerosol samples (see e.g., Duarte et a., 2021); it is ideal for heavy metals accurate quantification which is performed on solubilized samples by strong acid digestion thus requiring a time-consuming step, introducing a dependence on the extraction efficiency and possible sample contaminations, and destroying the filter sample. In addition, ICP-MS instruments need frequent calibrations and strict quality control checks to ensure stable and robust element detection. As far as aerosol source tracers are concerned, a major drawback of ICP-MS is the poor detection of elements like Si which is a key tracer for mineral dust particles (see e.g., Canepari et al., 2009; Niu et al., 2010).

It is well-known that the ED-XRF technique is characterized by higher minimum detection limits (MDL) compared to ICP-MS (up to two orders of magnitude; see e.g., Hyslop et al., 2024) and PIXE (up to one order of magnitude; see e.g., Calzolai et al., 2008); this is a limiting factor when very low aerosol loadings or trace/ultra-trace elements are of interest but e.g., for source apportionment purposes it proved to be effective also when analyzing sub-daily samples or size-segregated samples (see e.g., Bernardoni et al., 2011a; Bernardoni et al., 2011b). The filter type used for the aerosol samples also play a role in the technique performance as reported by previous literature works (see e.g., Calzolai et al., 2008; Ogrizek et al., 2022). As far as low Z elements are concerned, especially for heavy loaded samples (Hyslop et al., 2024), a limitation of techniques based on the detection of fluorescence X-rays is the matrix effect, whereby emitted X-rays are reabsorbed by other particles in the sample matrix or are self-absorbed within single coarse particles (Hunter, and Rhodes, 1972; Van Grieken and Markowicz, 1993) thus leading to an underestimation of the low-Z elemental concentrations. However, these effects can be properly taken into account using correction factors that can be either experimentally retrieved (see e.g., the use of PIGE-Particle Induced Gamma-ray

Emission analysis jointly with PIXE in Ariola et al., 2002; Calzolai et al., 2014) or by theoretical calculations (see e.g., Hunter and Rhodes, 1972a, 1972b; Criss, 1976; Foster et al., 1996).

PM samples are usually collected by air quality monitoring networks with a time resolution ranging from 24-h to one week, to ensure that enough PM mass is available for the analytical analysis, which is carried out in a laboratory. The elemental composition of PM is then obtained with a considerable time delay and at low temporal resolution. In recent years, there has been a growing interest in developing instruments for high temporal resolution measurements. Sampling at a high time resolution (1-h or less) allows to capture fast processes which aerosol particles are subjected to in the atmosphere and to retrieve information about the typical hours of activity of a certain source, leading to a better characterization of PM emissions. However, due to the short integration times, high-time resolution measurements are often close to the MDL of the analytical techniques (Malaguti et al., 2015).

Regarding the ED-XRF method, new systems have been developed which are able to sample PM particles with a sub-hourly or hourly time resolution and to automatically measure their elemental concentration, providing near-real time data access. These instruments are known as online XRF spectrometers and can be employed for long monitoring periods (months, years) at a site with the advantage of requiring limited maintenance. However, their high cost may prevent the simultaneous use of multiple devices at different sites or the investigation of different size classes (Furger et al., 2017). One of these advanced instruments is the Xact® 625i Ambient Metals Monitor by Cooper Environmental (USA), which performs in situ automated measurements of the elemental concentration of PM with a user selected time resolution ranging from 15 to 240 min. During operation, remote access to the data is available, enabling continuous, near-real-time monitoring of the instrument and ambient metal concentrations. Although the Xact® is currently one of the most widely used online ED-XRF analyzers, it is worth noting that other instruments with similar working principles are also available, such as the Horiba PX-375 ED-XRF monitor, whose setup and performance are described in detail in Asano et al., (2017) and Trebs et al., (2024).

The Xact® 625i and its forerunner versions have been successfully employed in several field studies in the past years, which compared its online measurements to daily samples analyzed with more established laboratory techniques (Bhowmik et al., 2022; Tremper et al., 2018; Furger et al., 2017; Park et al., 2014; US-EPA, 2012). Among these studies, only in Park et al., (2014) the daily filters were analyzed with the ED-XRF technique; in all the other cases, the elemental concentration of daily samples was retrieved with ICP-MS and ICP-OES (inductively coupled plasma optical emission spectrometry). In the latest cases, the comparison was then influenced by the different choice of the analytical technique. Moreover, in most of these studies, the experimental campaigns were carried out only for a few weeks/months, leading to a very limited number of points available for the intercomparison. An evaluation of the performances of Xact® 625i (compared with the ICP-MS technique) during different seasons was conducted only by Bhowmik et al., (2022) who conducted the field campaigns during summer (June-July) and winter (October-December) 2019 at two sites in Delhi.

In this study, an Xact® 625i monitor was deployed for nearly 6 months (July-December 2023) in Milan (Po Valley, Italy) at a monitoring station of the Lombardy Regional Agency for Environmental Protection (ARPA Lombardia), where air quality measurements are performed continuously. Xact® 625i hourly samples measured online with ED-XRF were compared to daily filters measured offline by ARPA Lombardia with a benchtop ED-XRF spectrometer in their laboratory. The goals of this paper are (1) to assess the on-line instrument performance in typical summer and winter elemental concentration ranges for PM_{10} collected at an urban background site in the Po valley (Italy); (2) to evaluate the quality of the obtained data for the selected elements in relation to their MDLs; (3) to quantify the data robustness based on intercomparison between Xact® 625i and elemental concentrations provided by a benchtop ED-XRF spectrometer.

2. Materials and methods

2.1 Site characteristics

The field campaign was performed at the permanent station Milano Pascal of the ARPA Lombardia Air Quality Network from 6 July until 12 December 2023. This is an urban background site located in the eastern side of Milan, in the University campus area called "Città Studi" (45.478°N, 9.231°E; 122 m a.s.l); the station is placed in a public park about 130 m from road traffic. The metropolitan city of Milan is the second most densely populated area in Italy (ca. 2300 inhabitants km^{-2}, almost doubled by daily commuters) and is located in the Po Valley, a well-known European pollution hotspot. The site is characterized by wintertime episodes of high pollutant concentrations, due to emissions from a variety of sources (e.g., residential heating, traffic, and industries) and prolonged atmospheric stability conditions related to the presence of the mountain chains of the Alps and the Apennines (Vecchi et al., 2007, 2009). Moreover, in Milan more than 80% of the days in a year are characterized by wind speed lower than 2 m s^{-1} (Vecchi et al., 2019). The site is well documented with respect to gas-phase pollutants (e.g. NO_x, SO_2, O_3), PM_{10} and $PM_{2.5}$ chemical characterization, and source apportionment (e.g., Amato et al., 2016; Altuwayjiri et al., 2021).

2.2 Xact® 625i

The Xact® 625i Ambient Metals Monitor (Cooper Environmental Services (CES), Beaverton, OR, USA) is an online energy dispersive XRF spectrometer, designed for continuous measurements of the elemental composition of ambient aerosol. The device operates using a reel-to-reel filter tape sampling technique, followed by the analysis of metals in the resulting PM spot through energy dispersive X-ray fluorescence (ED-XRF). Ambient air is drawn inside the instrument through a PM size-selective inlet which was PM_{10} in this study, with a flow rate of 16.7 lpm and the PM is collected onto a Teflon filter tape. After each sampling interval is completed, the filter tape is automatically advanced to the XRF system, where the resulting PM deposit is irradiated with an X-ray tube (rhodium anode, max voltage: 50 kV, current:1 mA) with three excitation conditions (see Table S1 in the Supplementary Material) and the fluorescence X-rays are measured by a silicon drift detector (SDD). In the meantime, the next sample is collected on a clean spot of the filter tape and the process is repeated during each sampling interval, which was set at 60 min for this study. The XRF spectra thus produced are automatically analyzed by a proprietary software for spectral analysis and elemental quantification which is installed on the built-in computer. The software, through a linear least-squares deconvolution algorithm, fits each measured spectrum with a library of pure element reference spectra to obtain the concentration data for each calibrated element in ng m^{-3}. Data can be then downloaded and monitored remotely with an internet connection. Sampling and XRF analysis are performed continuously and simultaneously, except for the time required for tape advancement (~ 20 s). Quality assurance (QA) checks are performed every day at midnight for 30 min and consist of an energy calibration (using a rod coated with Cr and Nb) and an upscale measurement to monitor the stability of the instrument response (for Cr, Pb, and Cd). Therefore, the sample following midnight is collected with a sampling interval limited to 30 min (00:30-01:00 LT).

The instrument was located inside a temperature-controlled cabinet outside the ARPA Lombardia monitoring station. If any errors are detected during operation, the system halts sampling, ramps the X-rays down for safety, and displays the cause of the error. The instrument was configured to quantify 36 elements: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Cd, In, Sn, Sb, I, Ba, Hg, Tl, Pb, and Bi; in addition, Nb is also detected for daily QA checks. Before the beginning of the experimental campaign, each of these elements was calibrated with a reference standard sample. For each element, 1σ interference-free MDLs ($MDL_{1\sigma}$) for 1-h of sampling are reported in Table S2, provided for Xact® 625i following the approach reported in Currie (1977). In XRF analyses, MDLs are inversely proportional to the square root of the irradiation time, which in the case of Xact® 625i corresponds to the sampling interval. Therefore, lower MDLs are reached for longer sampling durations.

2.3 Daily PM_{10} filter samples

Daily PM_{10} samples were collected on mixed cellulose ester membrane filters (47 mm diameter) with a SWAM Dual Channel Monitor (FAI Instruments, Rome, Italy) equipped with PM_{10} and $PM_{2.5}$ inlets. The elemental composition of PM samples was determined offline by ED-XRF spectrometry in the laboratories of the Environmental Monitoring Sector of ARPA Lombardia. An Epsilon 4 spectrometer from Malvern Panalytical (Monza, Italy) was used for the ED-XRF analysis. Four different irradiation conditions, which are reported in Table S3, were chosen to optimize the measurement of 19 elements, i.e., Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, and Pb. For these measurements, MDLs based on 24-h sampling time were evaluated as three times the square root of the counts in the background below the peak of the element divided by the corresponding sensitivity in the blank filter ($MDL_{3\sigma}$) (Jenkins, 1981; Lindgren, 2006) and are reported in Table S4.

2.4 Data coverage

The Xact® 625i measurements started on 6 July 2023 16:00 LT (local time) and ended on 12 December 2023 22:00 LT. The sampling interval of the instrument was set to 1-h. During the summer, in July and August, Xact® 625i suffered from high temperatures during the heatwaves, causing the X-ray tube to reach temperatures above 45° C. This led to automatic shutdowns of the measurements and to subsequent manual restarts, mostly performed remotely. The issue was mainly observed in the central hours of the day, from 13:00 to 16:00 LT. Nevertheless, it was still possible to attain a data coverage above 80% for Xact® 625i data in the central hours of the day during summertime. As a precautionary measure to avoid heat damage to the X-ray tube, Xact® 625i was switched off from 12 to 24 August. During those days, a power failure in the ARPA Lombardia cabin caused also the interruption of daily measurements. Another power failure occurred from 22 October to 8 November, leading to a long pause of hourly measurements. The X-ray tube of Xact® 625i started malfunctioning on 6 December. The issue could not be resolved and the X-ray tube had to be replaced, resulting in a premature end of the experimental campaign.

Overall, the Xact® 625i dataset consists of 2693 valid 1-h samples out of 3822 possible samples, attaining a coverage of 70%. For the daily filters, the dataset consists of 149 samples out of 157 possible samples, reaching a coverage of 95%. A timeline of the periods in which data are missing is reported for both hourly and daily measurements in Figure S1. A summary of the periods of interruption of the measurements lasting more than 12 hours is reported in Table S5. The number N of overlapping days with validated data is reported in Table 1 for each element considered for the intercomparison.

Xact® 625i data, which were originally reported in LT, were synchronized to daily samples and expressed in UTC+1 time zone.

2.5 Treatment of data below MDLs

Following the approach of Furger et al., (2017) and Tremper et al., (2018), for the intercomparison study here presented the $MDL_{3\sigma}$ was considered also for Xact® 625i; indeed, the $MDL_{3\sigma}$ assures a high statistical confidence (99.7%) and a better comparability with previous literature works. Hereafter, $MDL_{3\sigma}$ will be referred simply to as MDL.

All the elements measured on the daily filters by offline ED-XRF have less than 35% of their data points below their MDL. Among the elements detected by Xact® 625i, 13 of them (P, Co, Ga, Ge, Y, Cd, In, Sn, Sb, I, Hg, Tl, and Bi) have more than 90% of their data points below MDL; therefore, these elements were excluded from the intercomparison analysis. V and Rb have >70% of their data points below MDL leading to a less robust intercomparison with offline ED-XRF (see Figure S2). In Table S6, the number of data points with concentrations above the MDL is reported for each element measured by Xact® 625i and by offline ED-XRF.

The intercomparison between Xact® 625i and daily PM_{10} elemental concentrations was finally performed on 16 elements (Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb) which were measured by both techniques and were consistently above their MDLs.

3. Results and discussion

3.1 Data overview

An overview of the data recorded during the experimental campaign is given in Fig. 1, taking into account all available valid data of the elements considered for the intercomparison. To account for seasonal differences in terms of meteorology and emissions, data were divided into 3 periods: July-August, September-October and November-December. The basic statistics of the dataset, including the mean, median, standard deviations, 25th and 75th percentiles are reported in Table S7. As previously mentioned, the Xact® 625i data coverage for July and August was impacted by the loss of data mainly related to the time interval 13:00-16:00 LT when hot temperatures caused the X-ray tube switch-off; therefore, the statistical robustness of the comparison is lower than in the other represented periods.

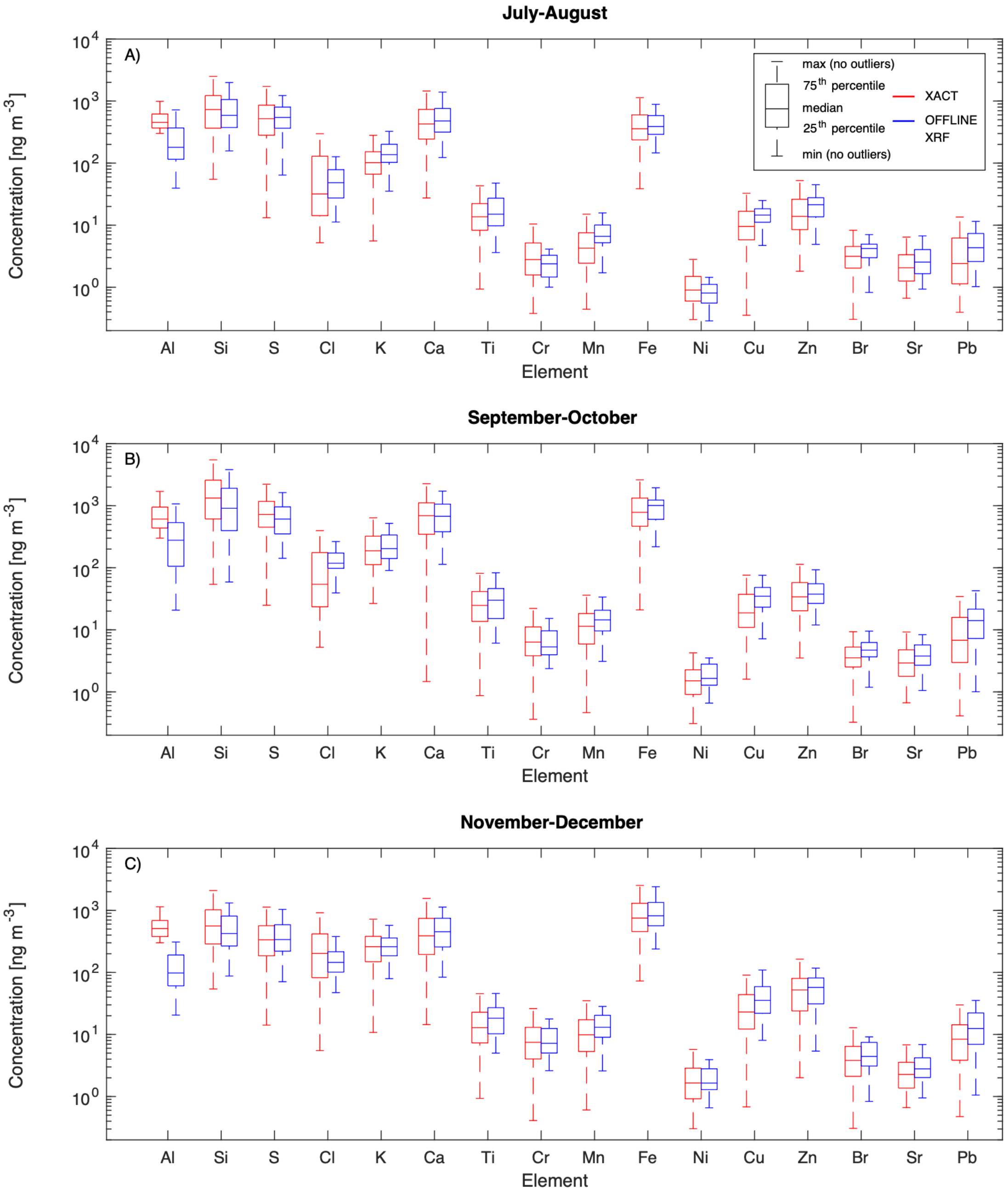

Figure 1: Box plots of the concentrations for the elements considered for the intercomparison, measured hourly online (in red) and daily offline (in blue) during the experimental campaign in (a) July-August, (b) September-October, and (c) November-December. The bottom and the top of each box are the 25th and 75th percentiles, respectively; the line in the middle of the box is the median; the bottom and top whiskers are the minimum and maximum value respectively.

3.2 Intercomparison data analysis approach

For the intercomparison between the two methods, Xact® 625i hourly data were averaged to 24-h to be comparable to the corresponding daily filter samples measured by offline ED-XRF. Every day, during QA checks performed from 00:00 to 00:30 LT, Xact® 625i generates one sample with a 30-

min time resolution so that this sample is added to the 23 hourly samples to calculate 24-h daily means. This procedure implicitly assumes that the half-hour sample collected during the first hour of sampling is representative of the entire hour. The hypothesis was tested conducting 23.5 h weighted means on a small number of samples, following the method of Furger et al., (2017). Tests showed a difference of less than 3% between the 23.5 h weighted mean and the 24-h mean, which was then chosen as calculation method. For this reason, Xact® 625i data were aggregated to 24-h daily means. As previously stated, during the campaign summer days were affected by heat waves, which caused Xact® 625i to stop during the central hours of the day, leading to missing data. For this reason, the data coverage of Xact® 625i was evaluated for each day of the experimental campaign. In order to avoid misestimation of daily Xact® 625i concentrations, days with less than 18 hourly valid data (75% coverage) were excluded from the intercomparison. In addition, Xact® 625i daily means were not calculated when more than 6 hourly data were under the MDL for one day. In all comparisons, data under MDL were replaced by 0.5·MDL.

The comparisons between the daily PM_{10} elemental concentrations retrieved by ARPA Lombardia through offline ED-XRF and the daily means calculated from Xact® 625i hourly data were carried out using the Deming regression (Deming, 1943). This regression approach minimizes the sum of distances between the regression line and the X and Y variables, considering the experimental uncertainties in both variables. For the offline ED-XRF measurements, the uncertainty included contributions of 5% from calibration standard uncertainty (U.S. EPA, 1999) and, for each spectrum, the contribution of counting statistics and fitting errors. For the Xact® 625i measurements, the uncertainty included contributions of 5% from calibration standard uncertainty (U.S. EPA, 1999), and an element-specific uncertainty derived from the spectral deconvolution calculated by the instrument software for each spectrum, which includes also the contribution of the flow and the sample deposit area. The mean relative uncertainties registered during the experimental campaign are reported for each element and for both online and offline methods in Table S8.

3.3 Intercomparison results

The results of the intercomparison between the PM_{10} elemental concentrations retrieved offline and online are reported in Table 1. The Deming regression parameters are reported along with their uncertainties and the coefficient of determination of the linear regression; the number of data (N) considered for the comparison after data reduction is also reported.

Element	Slope ± uncertainty (online vs offline)	Intercept ± uncertainty [$\mu g\ m^{-3}$] (online vs offline)	N	R^2
Al	1.29 ± 0.22	0.1640 ± 0.0917	42	0.83
Si	1.69 ± 0.13	-0.2528 ± 0.1003	97	0.94
S	1.25 ± 0.02	-0.0469 ± 0.0070	101	0.99
Cl	1.69 ± 0.25	-0.0493 ± 0.0290	75	0.67
K	1.05 ± 0.03	-0.0207 ± 0.0054	102	0.97
Ca	1.03 ± 0.03	0.0038 ± 0.0169	102	0.95
Ti	1.00 ± 0.06	-0.0006 ± 0.0011	100	0.96
Cr	1.30 ± 0.08	0.0014 ± 0.0004	77	0.86
Mn	0.83 ± 0.02	-0.0002 ± 0.0003	101	0.95
Fe	0.96 ± 0.02	0.0385 ± 0.0118	102	0.98
Ni	0.79 ± 0.06	0.0004 ± 0.0001	79	0.87
Cu	0.85 ± 0.01	0.0006 ± 0.0002	102	0.99
Zn	0.98 ± 0.02	-0.0001 ± 0.0008	102	0.99
Br	1.06 ± 0.04	-0.0006 ± 0.0002	96	0.96
Sr	0.98 ± 0.06	-0.0008 ± 0.0002	74	0.97
Pb	0.94 ± 0.03	-0.0017 ± 0.0003	83	0.99

Table 1: Deming regression results and coefficient of determination for the comparison between Xact® 625i (Y) and offline ED-XRF data (X). For each element, the number of points (N) available for the intercomparison is reported.

The scatterplots of the intercomparisons are presented in Figures 2-5. The time plots of the time series obtained by the two measurements methods are reported in Figures S3-S6. The 16 selected elements are compared by dividing them into three groups based on data characteristics.

The first group, Group A (Figures 2-3), includes K, Ca, Ti, Fe, Zn, Br, Sr, and Pb. This group shows excellent correlation between the two measurements methods (R^2 >0.95) and is characterized by slopes compatible to unity within three times the uncertainty of the fitted slope (3σ). For Ca, Ti, and Zn also the intercepts are compatible to 0 within 3σ. Among this group, K, Ca, Ti, Fe, and Zn, are measured by Xact® 625i with relative uncertainties in the range 10-20% (see Table S8). Br, Sr, and Pb are instead measured by Xact® 625i with a higher uncertainty, on average 30-50% (see Table S8), and Sr and Pb hourly data are also more frequently under the MDL (20% of data).

The second group, Group B (Figure 4), consists of the elements Si, S, Mn, and Cu. This group is characterized by excellent correlation between the two measurements methods (R^2 >0.95) but, in contrast to Group A, the slopes of the regressions are not compatible to 1 within 3σ. Si and S are among the lightest elements measured by Xact® 625i and, along with Al, it can be tricky to measure with ED-XRF because of absorption effects due to the presence of air in the irradiation chamber (e.g. as typically occur in the XRF online measurements) and/or self-absorption inside the coarse particles themselves (Hunter, and Rhodes, 1972; Van Grieken and Markowicz, 1993); these effects can lead to an underestimation of low-Z element concentrations. Nevertheless, looking at the results for Al, Si, and S, absorption effects seem not to be the cause of the observed discrepancy as Xact® 625i data are typically higher than offline ED-XRF analysis. Moreover, it should be noted that Si is detected by Xact® 625i with mean uncertainties of 30%, while S is detected with mean uncertainties of 10%. In the case of Mn and Cu, concentrations provided by Xact® 625i are constantly lower than daily offline measurements by approximately 15%.

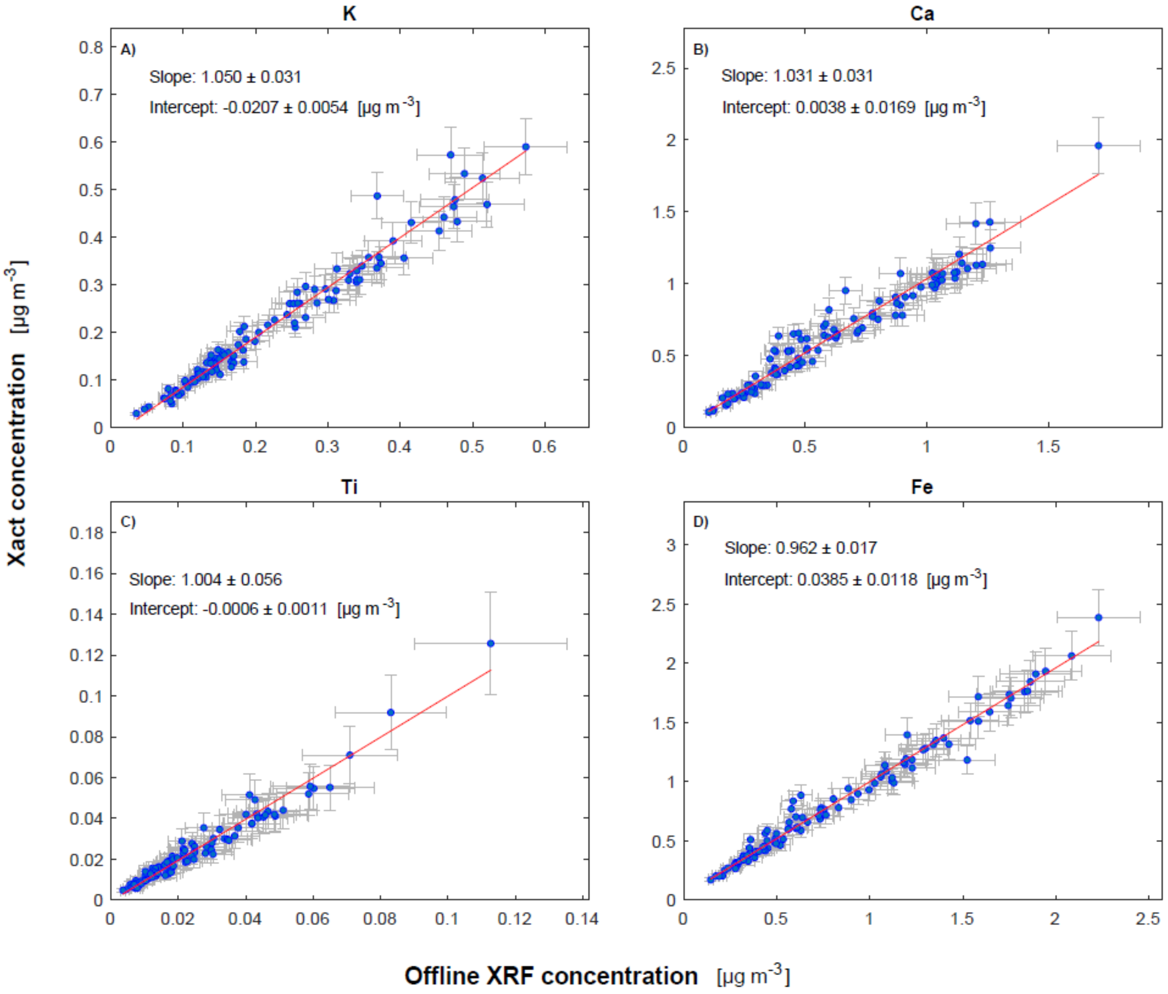

Figure 2: Scatterplots of the intercomparison between Xact® 625i data and offline ED-XRF data for the elements K, Ca, Ti, and Fe of Group A. The error bars represent the mean experimental uncertainties reported in Table S8.

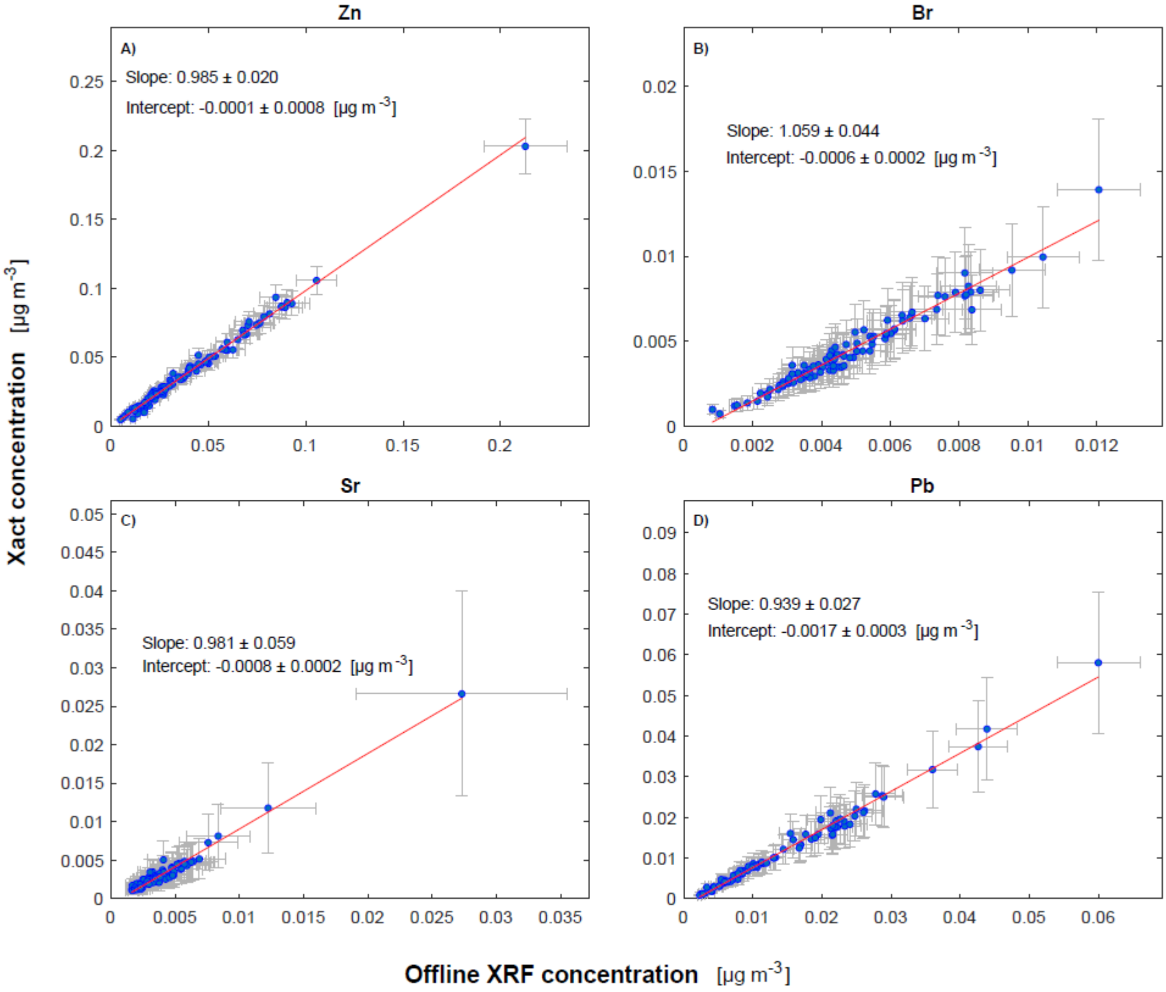

Figure 3: Scatterplots of the intercomparison between Xact® 625i data and offline ED-XRF data for the elements Zn, Br, Sr, and Pb of Group A. The error bars represent the mean experimental uncertainties reported in Table S8.

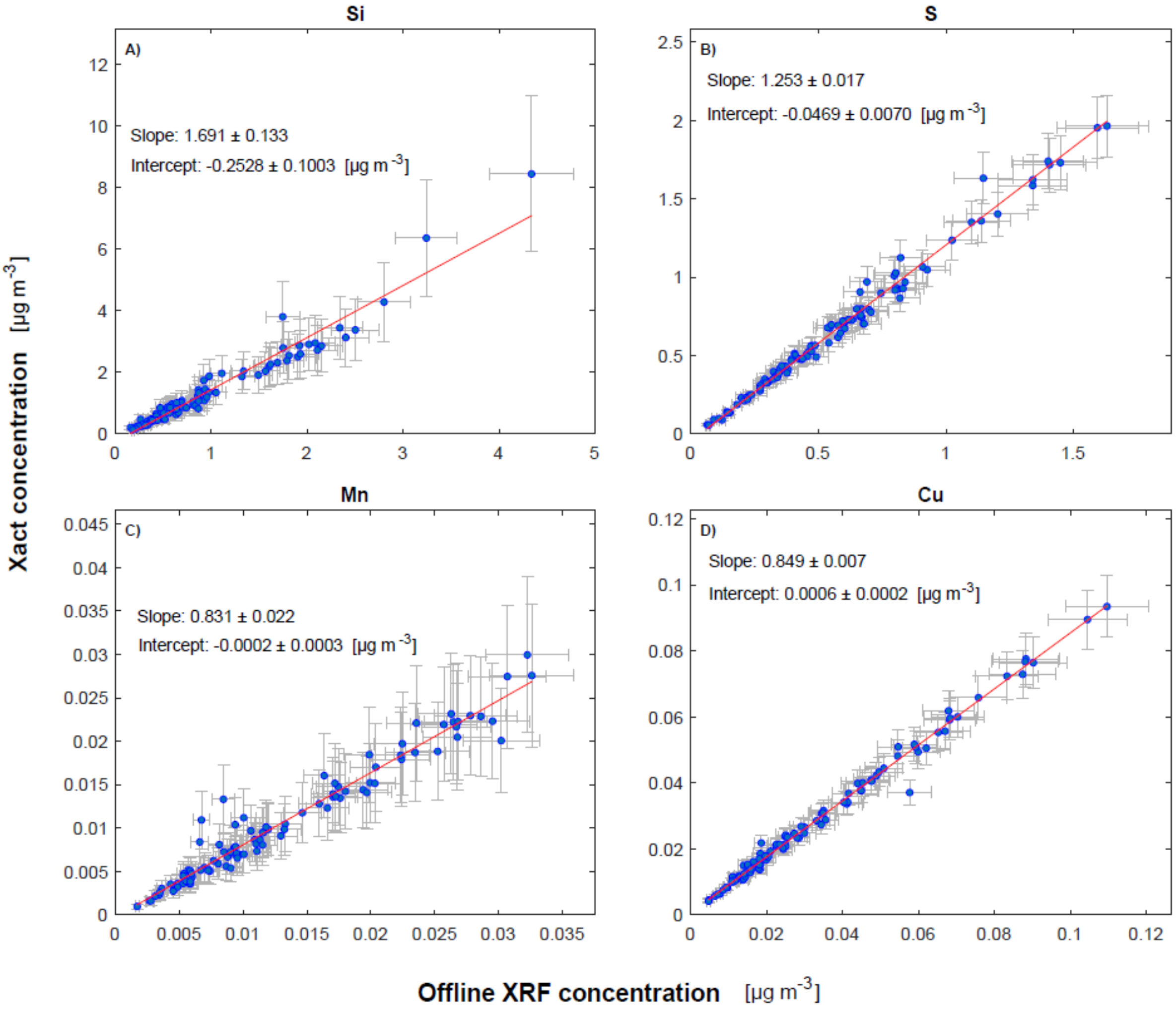

Figure 4: Scatterplots of the intercomparison between Xact® 625i data and offline ED-XRF data for the elements of Group B: Si, S, Mn, and Cu. The error bars represent the mean experimental uncertainties reported in Table S8.

A possible explanation for the observed discrepancies is related to the fact that, despite all samples are measured through ED-XRF technique, the spectra analysis for quantitative analysis is different and – more importantly - the two instruments are not calibrated with the same set of certified standards, which can lead to different quantification of concentrations. However, Xact® 625i data of the elements of this group can still be validated when compared to an offline measurement technique and used for high-time resolution elemental concentrations assessment, after harmonisation of the datasets.

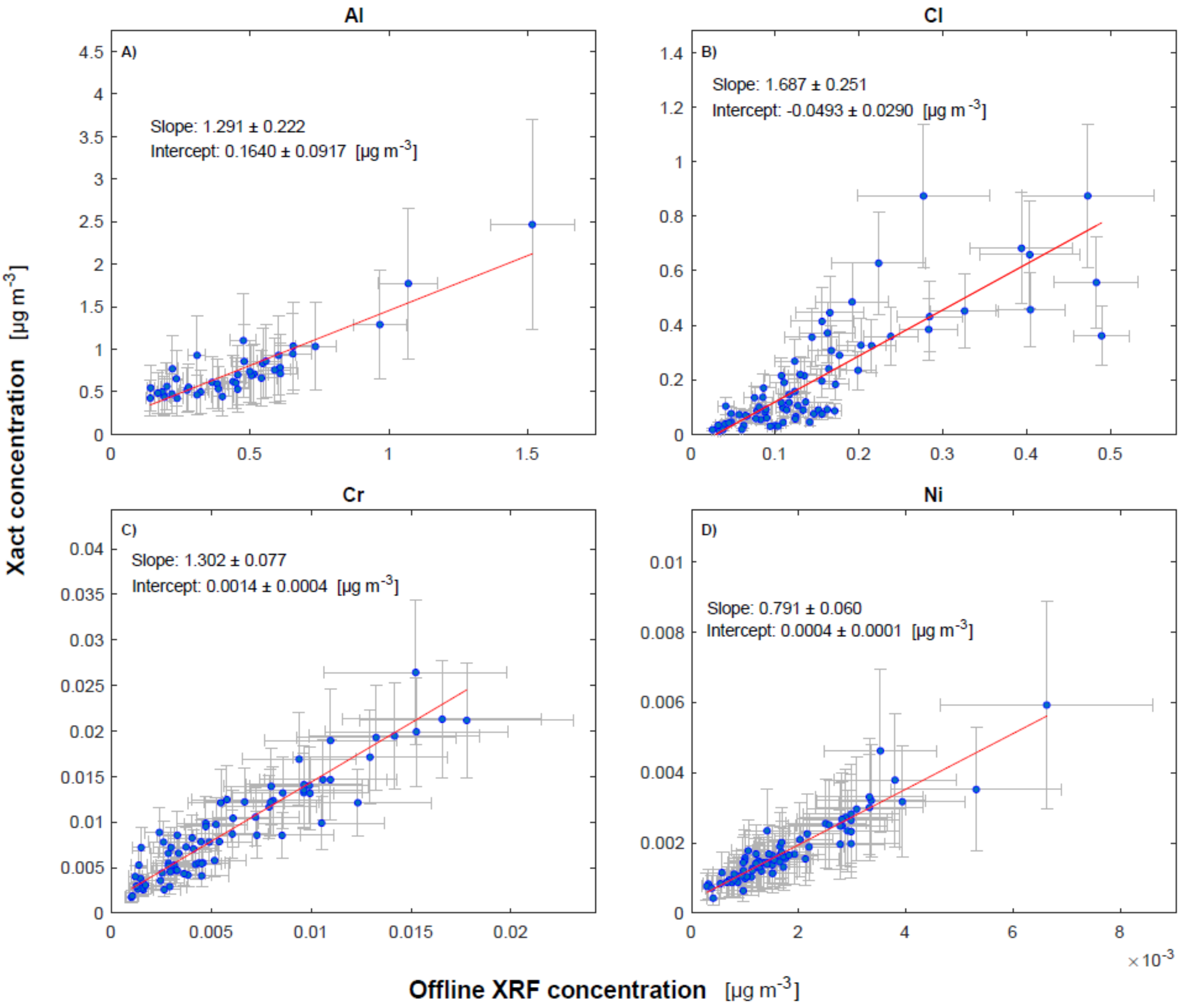

Figure 5: Scatterplots of the intercomparison between Xact® 625i data and offline ED-XRF data for the elements of Group C: Al, Cl, Cr, and Ni. The error bars represent the mean experimental uncertainties reported in Table S8.

The third group of elements, Group C (Figure 5), is composed of Al, Cl, Cr, and Ni. This group shows less comparability between the two methods, with R^2 in the range 0.67-0.87. Cl, Cr, and Ni are frequently close or under the MDL for both experimental techniques and are characterized by mean relative uncertainties in the range of 30-50%. For these elements, the comparison could be improved by carrying out the Xact® 625i measurements on a 2 h time scale. Among the 16 elements evaluated for the intercomparison, Al is the one with the highest MDL for Xact® 625i hourly measurements and its hourly concentrations are under the MDL for nearly 35% of data points, while Al offline data are always above the MDL. Al is also measured by Xact® 625i with mean uncertainties of 50%. As can be seen also in Figure S6a, the Xact® 625i time series of Al is characterized by a constant upward shift in background concentrations, which is not observed for the other elements. The measurement of Al with Xact® 625i is complicated by the fact that the instrument uses an Al filter to carry out the analysis, as reported in Table S1; another possible issue could be that the X-rays hit some internal parts of the instrument, causing a significant increase of the background. Al concentrations cannot thus be corrected in a reliable way and further improvements in the instrument should be considered to enhance Al detection. In the case of Cl, which shows quite scattered data, concentrations obtained by Xact® 625i are on average higher than the ones measured offline on daily samples. This could be explained by the volatility of Cl. Xact® 625i ED-XRF measurements are performed immediately after the collection of the sample, while daily PM_{10} filters are stored in the sampler at the monitoring station for up to 2 weeks before being taken to the laboratory for the offline ED-XRF analysis.

The results of this study represent a significant step forward from Park et al., (2014), which is – as far as we know - the only previous study available in literature presenting a comparison between Xact® hourly data and offline ED-XRF daily data. Park et al., (2014) conducted an experimental campaign with a forerunner version of Xact® (Xact® 620) in Gwangju, South Korea. The campaign was carried out during February 2011 and lasted only 1 month, focusing on the $PM_{2.5}$ fraction. The Xact® 620 model, was the first commercially available near real time ambient metals monitor; it was able to detect elements starting from K and had higher detection limits (details can be found in Park et al., 2014), required more manual intervention for calibration and quality assurance processes and had a more basic interface with limited remote access capabilities. The daily filters were measured offline with an Epsilon 5 ED-XRF spectrometer (Malvern Panalytical). The study compared the online and offline concentrations of 12 elements (K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, As, Ba, Pb), 9 of which were also analyzed in our study. For the 9 common elements (K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb), they observed a mean R^2 of 0.89 and a slope of 1.31, with Xact® measurements on average 30% higher than offline ED-XRF. In our study, for these 9 elements, we found a much better correlation, with a mean R^2 of 0.96 and slope of 0.94, which is closer to unity. Moreover, our study included also 7 elements (Al, Si, S, Cl, Cr, Br, Sr) which were not taken into account by Park et al., (2014), and the measurement campaign lasted for a longer period (6 months), giving more robustness to the results.

Overall, considering all the 16 elements evaluated in this study, we found a good correlation (mean R^2 of 0.93) between the online and offline ED-XRF, with a mean slope of 1.11. The results are also in agreement with Tremper et al. (2018), which compared Xact® measurements to ICP-MS daily measurements in three sites in the United Kingdom. They observed a mean R^2 of 0.93 and a slope of 1.07 for the elements As, Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Sr, Ti, V, and Zn. In the study by Furger et al. (2017), they found instead that the elemental measurements by an Xact® 625i were on average 28% higher than ICP-OES and ICP-MS measurements for S, K, Ca, Ti, Mn, Fe, Cu, Zn, Ba, and Pb.

A summary of previous literature studies and their characteristics is reported in Tables S9 – S10. In these studies, several reasons for the differences observed between the Xact® data and the offline techniques are described and some of them are shortly reported below. In general, as specified in Tremper et al., (2018), the measured elements are chosen to represent a range of source categories (i.e. regulatory, traffic, industry), plus the internal standard (Pd for Xact® 625 and Nb for Xact® 625i). The number of elements that are actually quantified and thus included in the intercomparison results for each study depends on the ambient air concentrations, and thus the site, and MDL of the techniques.

In the US-EPA (2012) work, intercomparison results are available only for 6 elements, as the others were under the MDL of ICP-MS analysis and/or Xact® measurements; weak regression parameters for Cu are explained by concentrations frequently close to MDL of both techniques. In Furger et al., (2017), Xact® and ICP-MS data showed high linearity and little scatter in the regressions for the elements S, K, Ca, Ti, Mn, Fe, Cu, Zn, Ba, and Pb; the relative mean difference of 28% they have found was attributed to many possible causes such as differences in the inlets used for the Xact® and the high-volume samplers for ICP-MS filter samples, a slightly different location of the samplers, possible calibration issues with the Xact® for S, values next to MDLs for one or both techniques, XRF particle-size-dependent self-absorption effects for the lighter elements, and line interferences or contaminations during the ICP-MS digestion and analysis procedures. Tremper et al. (2018) and Bhowmik et al. (2022) both mentioned similar reasons for the differences observed between Xact® and ICP-MS filter data; in addition, blank filters were found to be variable, the standards used for Xact® calibration had a much higher concentration than ambient air and the calibration matrix differed from the sample matrix.

4 Conclusions

This study was realized to evaluate the performances of an Xact® 625i online energy dispersive XRF spectrometer. Although X-ray fluorescence is notably less sensitive than other analytical techniques like ICP-MS, it is robust and stable so that online spectrometers can be deployed also in monitoring networks due to easy use and little maintenance. Online spectrometers are still quite expensive and only a reduced number of elements are detectable compared to e.g., ICP-MS but for source apportionment studies the availability of high resolution elemental composition is currently key to refined modelling applications. Indeed, the possibility of joining high-time resolution, which provide details on temporal patterns, and low-time resolution elemental data, which allow the detection of elemental tracers for specific sources, has been already proved to be effective for source apportionment studies (see e.g., Crespi et la., 2016; Forello et al., 2019; Mooibroek et al, 2022).

A six-month experimental campaign was carried out at the ARPA Lombardia monitoring station Milano Pascal (Milan, Italy) from July to December 2023. The instrument was configured to continuously measure 36 elements, ranging from Al to Bi, with 1-h time resolution. The measurement quality of Xact® 625i was tested by intercomparison with ED-XRF offline analyses on 24-h PM_{10} samples with a well-established benchtop spectrometer. Xact® 625i hourly data were aggregated to 24-h means and compared to daily PM_{10} data. The study focused on 16 elements which were measured by both techniques and were consistently above their MDLs (Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb).

Xact® 625i was found to be a highly reliable instrument, suitable for measurements of elemental concentration of PM_{10} in summer and winter conditions at 1-h time resolution. Xact® 625i elemental concentrations were found to be highly correlated to the offline ED-XRF analyses of the daily samples (R^2 in the range 0.67-0.99) albeit with slopes ranging from 0.79 to 1.70. Elements were divided into three groups according to their characteristics. The first group, Group A (K, Ca, Ti, Fe, Zn, Br, Sr, and Pb), shows excellent correlation between the two measurements methods ($R^2 > 0.95$) and slopes compatible to 1 (range 0.94-1.06). Group B (Si, S, Mn, and Cu) is still characterized by excellent correlations between the two techniques, but the regression slopes are not compatible to 1. Xact® 625i performances are more critical for the elements of Group C (Al, Cl, Cr, Ni). These elements are frequently under the MDL for one or both experimental techniques and show the worst correlations between the two methods (R^2 ranging from 0.67 to 0.87). An issue of the Xact® 625i instrument is related to the quantification of Al, which is problematic so that the Al concentrations are basically not reliable.

Future work should include an intercomparison between an Xact® 625i and an offline ED-XRF spectrometer calibrated with the same certified standards, in order to avoid biases linked to the calibration of the instruments. Moreover, it would be interesting to assess the reliability of Xact® 625i high time resolution measurements by comparing it to other instruments/technique able to perform measurements of PM elemental concentration at high time resolution, like Horiba PX-375 ED-XRF automatic sampler (Asano et al., 2017; Trebs et al., 2024).

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Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

The Department of Physics of the University of Milan is acknowledged for the fellowship provided to Laura Cadeo.