Elemental characterization and risk assessment of indoor aerosols in an electrostatic particle accelerator laboratory

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ABSTRACT

Aerosol samples (PM$_{10}$ and PM$_{2.5}$) were collected during the 2018-2019 dry-cold season, inside an electrostatic particle accelerator laboratory at Instituto de Física, Universidad Nacional Autónoma de México, and on the rooftop. The goal was to measure gravimetric mass and elemental concentrations, to identify emitting sources, and to assess risks to human health due to inhalation, ingestion and dermal deposition, through Hazard Quotients. Concentrations of Mg, Al, Si, P, S, Cl, K, Ca, V, Mn, Fe, Ni, Cu, and Zn were measured with X-ray Fluorescence. Mass concentrations were lower indoors than outdoors. Elemental/gravimetric mass concentrations ratios showed that S, Ni, Cu, and Zn were more abundant in both indoors particle sizes, plus P in PM$_{2.5}$. Possible sources, found through Cluster Analysis, were geogenic, SF$_{6}$ subproducts, vacuum pump oil, and air conditioning, supported by Scanning Emission Microscopy and Electron Probe Microanalysis. Health risks due to enriched elements are not significant.

1. Introduction

Air pollution is a global issue that affects climate, ecosystems, human health, and physical infrastructure (buildings, equipment, and cultural heritage). Therefore, it is necessary to perform studies aimed to assess its levels at different scales: the entire globe, regions, megalopolis or smaller cities. Besides, as people nowadays spend nearly 90% of their time in closed environments [1], it is mandatory to characterize air pollution in these places [2,3]. Among all the indoor air pollutants, particulate matter (PM), sulfur dioxide (SO$_2$), and nitrogen dioxide (NO$_2$) have been considered as the major risk factors for ill health and death [4], and the exposure to PM is associated with acute and chronic adverse health effects [4]. As a consequence, there are many works about the chemical properties, concentrations, and possible health effects of the pollutants in various indoor locations. Examples are classrooms [5,6], dental premises [7], offices [8–10], restaurants [11], industries [12–14], and households [15–20]. Nevertheless, very little investigation on this issue has been carried out in universities, industrial or research laboratories [21–24], although it has been observed that the concentrations of certain elements are higher inside the laboratories than in other university buildings [25].

The relevance of quantifying elemental concentrations and assessing its associated health risk has been demonstrated by many authors. For instance, Zhao X et al. [22] determined the exposition risk indices for As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, which are metals present in the indoor dust of a university library in China; Liu et al. [26], determined the Hazard Quotients due to PM$_{2.5}$ and PM$_{10}$ exposition for As, Cr, Cd, Ni, Co and Pb, at outdoor environments in several cities in China; Embiale et al. [27] estimated the concentration of trace elements and assessed the risk in adults for PM$_{2.5}$ present in a classroom; Maruthi et al. [28] assessed the human risk from trace elements present in PM$_{10}$ during food cooking with charcoal, kerosene and electric stoves in Ethiopia; Diaz et al. [29] calculated the risk from PM$_{2.5}$ inhalation for S, Cl, Ti, V, Cr, Mn, Ni, Cu, Zn and Pb in an elementary school in Mexico City.

Furthermore, it has been observed that the composition of air pollutants, especially particulate matter, is different in outdoor environments than in interiors, or that there may be a strong interaction between both of them. For instance, Rasmussen et al. [30] measured lower concentrations of fine particle inside Canadian homes than outside, while coarse particles had very similar mass concentration and elemental composition both indoors and outdoors. Amato et al. [31] observed that about 45% of indoor fine particles were produced inside classrooms in Barcelona, while the rest was transported from outside. Martuzevicius et al. [16] observed that traffic-related particulate matter has a strong influence in residential houses. In many countries, airborne particles represent a high risk in domestic indoor environments, due to the extended use of...
biomass-burning stoves, producing soot and toxic compounds [19,32]. These examples show that each environment may present different behaviors, depending on its location and the activities carried out inside. The health risks of indoor air pollutants are mainly due to the high concentrations caused by poor ventilation, inducing a bad indoor air quality, which can reduce the mental, physical, and social ability of a person, thus affecting work efficiency and productivity [33].

In a different issue, the International Atomic Energy Agency reports the existence of no less than 260 laboratories devoted to ion beam analysis, nuclear physics, or accelerator mass spectrometry around the world [34]. In particular, at the Instituto de Física, Universidad Nacional Autónoma de México (IFUNAM), a new accelerator facility has been operating since 2013, mainly for the application of accelerator mass spectrometry [35], that is officially known as Laboratory for Accelerator Mass Spectrometry (LEMA, in Spanish). This laboratory is based on a 1 MV High Voltage Engineering Europa (HVVE) tandem accelerator. As mentioned above, not much research exists about air pollution in laboratories, especially about airborne particulate matter (PM).

Moreover, it is convenient to assess the health risk due to the exposition of the personnel to the particulate matter, specifically regarding inhalation of some elements that characterize the composition of PM$_{10}$ in this closed environment [26,27,36,37]. PM$_{10}$ contains both fine and coarse fractions. The fine particles have a small mass and may stay suspended in the air for longer periods than the coarse fraction. While PM$_{10}$ can enter the upper respiratory tract, PM$_{2.5}$ may travel deeper until they reach the pulmonary alveoli. Also, along this trajectory, the fine particles may be adhered to the walls of the tract [29]. Therefore, risk assessment for both particle sizes is necessary in the present study.

Considering the personnel that works at LEMA and the required clean environment in the laboratory, it is important to investigate if the air quality inside the facilities is good enough for the experimental preparation and execution by the scientific staff. The present work is focused on the determination of the mass concentrations of particles with mean aerodynamic diameters smaller than 10 µm (PM$_{10}$) and 2.5 µm (PM$_{2.5}$) in the interior of the accelerator room and the use of X-ray Fluorescence (XRF) for elemental analysis of the collected particles, comparing the concentrations with those measured outdoors. Cluster Analysis (CA) was applied to the data set to associate each element with possible emitting sources. Therefore, the goal of this study is to identify elements with an increase of their concentrations as compared to the outdoor environment, to identify the sources, and to assess the risk to the personnel exposed inside the laboratory, due to PM$_{10}$ and PM$_{2.5}$ inhalation, ingestion, and dermal deposition.

2. Materials and methods

2.1 Sampling site

The accelerator room is sketched in Figure 1. Its dimensions are 10.9 m × 12.3 m × 5.0 m (width-length-height, respectively). The room has two access doors: one for the regular entry of personnel and the other one is only for introducing large equipment to the laboratory. None of them are usually open. The sampling device operated inside the accelerator room, near to the southeast corner. This site was selected because it is an area with minimal human interface, closed windows, and the air conditioning outlet is located at the opposite corner of the room (at a distance of nearly 16 m). Inside the laboratory, the accelerator occupies most of the space. The main components of the system are an ion source, a 1 MV Tandetron® accelerator, and two beam lines, for accelerator mass spectrometry and Nuclear Physics experiments. Additionally, there are six high vacuum systems that include mechanical vacuum pumps (model Trivac DBB-1, Leybold, Cologne, Germany) operating to maintain the vacuum in the accelerator and beamlines. It must be mentioned that both the accelerator and the air conditioning equipment operate continuously in the laboratory, unless and emergency occurs. Room temperature is maintained constantly at 21°C.

As explained by Reza et al. [38], there is a large number of research projects that require the presence of several researchers, staff, and students performing the experiments. The activities in the laboratory during a regular week (Monday to Friday) can be described as follows: from 7:00 h to 8:00 h, cleaning of floor and selected parts of the equipment; 9:00 h to 11:00 h, the accelerator is turned on and the samples to be analyzed are mounted in the ion source; 11:00 h to 19:00 h, normal operation, with no need for people to stay at

Figure 1. Scheme of the LEMA accelerator room, showing the location where the particulate matter sampler was installed.
the experiment room (which is radiation safe), although occasionally personnel installing equipment for future experiments enter the room for several hours. The accelerator is turned off around 20:00 h. Exceptionally, experiments are run 24 h or weekends, for example, when the number of samples is high or Nuclear Physics experiments are carried out [38]. None of the latter experiments occurred during the present study. Additionally, during the same dry cold season, PM$_{10}$ and PM$_{2.5}$ sampling was carried out in the roof of the building, to compare outdoor elemental concentrations with those determined in the laboratory.

2.2 Sampling equipment

The aerosol sampling devices were medium volume samplers (Ecotech AAS 271Mini, Ecotech Instruments, Kasna, India), which have two inlets to collect simultaneously PM$_{10}$ (at a nominal flux of 36 L min$^{-1}$) and PM$_{2.5}$ (the flux is nominally 16.67 L min$^{-1}$). The air inlets in this instrument are set at heights between 1.0 m and 2.0 m from the floor. The filtering media were either 3 µm pore size Teflon® (Pall Corp.) or 0.4 µm pore size polycarbonate (SPI-Pore) filters, both of a 47 mm diameter, depending on their availability. Both types have been shown to have a good performance for X-ray spectrometries, with no significant collection and analytical differences [39,40]. For the outdoor sampling, only Teflon® filters were used.

2.3 Sampling period

A total of 35 samples were collected indoor for almost 24 h, from 21 September 2018 until 16 January 2019, on business days. For quality assurance, one field blank filter was exposed for 24 h near the sampling site for every seven samples. Both gravimetrical and elemental concentration analyses were field blank corrected. Regarding the outdoor specimens, particulate matter samples were collected also during 24 h, also along the same days. Five field blank filters were collected, each one was exposed during seven sample change proceedings. The sample collection time covered from 9:00 h until 8:50 h of the next day, to allow filter changing.

2.4 Mass concentration

Both samples and field blanks filters were placed in Petri dishes and kept in a desiccator cabinet for 48 h before pre- and post-weighing with an Ohaus 200GD electrobalance (0.01 mg resolution). The operational conditions during gravimetric analyses were 35% RH and 21°C. External mass concentrations were also obtained from the Automatic Atmospheric Monitoring Network (RAMA) and the Manual Network (REDMA), both operated by the local government. PM$_{10}$ and PM$_{2.5}$ 24 h mean concentrations were measured at the REDMA Pedregal station (PED), located 2.8 km west of IFUNAM. Additionally, PM$_{2.5}$ hourly data were obtained from the closest RAMA station, located at the Centro de Ciencias de la Atmósfera (CCA), UNAM, 500 m north of the laboratory, to estimate any possible difference with the PED station.

2.5 Elemental analysis

Elemental concentrations were measured with an XRF spectrometer designed for environmental applications [41,42]. It is based on an Oxford Instruments (Mountain View, CA, USA) X-ray tube with Rh anode, operating at 50 keV and 500 µA. No filter at the exit of the tube was used for these analyses. The detection system consisted in an Amptek (Bedford, MA, USA) X-123DD spectrometer, with resolution of 120 eV at 5.9 keV. Finally, the system works under a high vacuum (10$^{-6}$ torr) provided by a turbomolecular vacuum pump (Turbovac ix/iX, Leybold, Cologne, Germany).

The X-ray detection system calibration was performed with a set of thin film standards, nominally 50 µg cm$^{-2}$, (MicroMatter Co, Vancouver, Canada) irradiated during 300 s under the conditions mentioned previously. Accuracy was evaluated with the National Institute of Standards and Technology (Gaithersburg, MA, USA) Standard Reference Material SRM-2783 (Air particulate on filter media). The details and results are thoroughly explained by Mejía-Ponce et al. [42]. Repeatability of the XRF system was verified by analyzing two thin film standards (Al and Fe) every day, with differences below 1% in the K$_{\alpha}$ X-ray peaks of both elements. Detection limits have been reported previously by Hernández-López et al. [43]. Finally, laboratory blank filters were analyzed every 10 samples and concentrations were blank corrected. Spectra for PM$_{10}$ samples and blanks were collected during 900 s and then integrated by means of the Quantitative X-ray Analysis System (QXAS) (IAEA 2007) [44]. Blanks were subtracted from sample concentrations and a correction due to the attenuation of emitted X-rays in the samples was also estimated [40]. The evaluation of experimental uncertainty for each elemental concentration (between 6% and 20%) is explained in the Appendix.

The resulting mass and elemental concentrations were subjected to a series of statistical analyses. Basic statistics, Analysis of Variance (ANOVA) and correlation matrices for mass and elemental concentrations were calculated with the Stata® software [45].

The possible identification of elements that may be enriched indoors as contrasted to those found outdoors, is carried out by comparing ratios of elemental mass to measured gravimetric mass, both indoors and outdoors. ANOVA is applied to these mass fractions to
to determine if the mean values are higher, due to increase of the elemental concentrations in the particles. Therefore, those elements can be associated to a possibly existing source inside the laboratory.

2.6 Cluster analysis

In order to recognize reasonable associations among the detected elements, Cluster analysis (CA) is applied to the PM$_{10}$ and PM$_{2.5}$ elemental concentrations data sets [46]. This was carried out by means of the Stata® computer code [45]. Ward’s method of amalgamation and Chebychev’s distance metric were employed to build dendrograms for PM$_{10}$ and PM$_{2.5}$, separately. It must be kept in mind that this analysis results only in qualitative grouping of the variables, so it will serve as a guide to identify the sources contributing to the presence of airborne particles indoors.

2.7 SEM analysis

Additionally, to exemplify some of the results obtained with XRF, several PM$_{10}$ and PM$_{2.5}$ samples deposited onto polycarbonate filters were analyzed with SEM. Images were obtained for different areas of the samples, and qualitative X-ray analyses with EPMA of selected particles was also done. These studies were completed at the Central Microscopy Laboratory (LCM), at IFUNAM, with a JEOL 7800 F scanning electron microscope.

2.8 Health risk assessment

The health risk posed by elements in PM$_{10}$ that may be enriched indoors for men and women were assessed, considering carcinogenic and non-carcinogenic effects, when applicable. In this work, only the Hazard Quotient (HQ) is evaluated. According to US EPA criteria [36], when HQ < 1 then non-cancerous effects are not highly probable; if HQ ≥ 1, undesirable health effects might occur. Finally, if HQ > 10, there is a high chronic risk to human health. Moreover, the US EPA establishes a tolerable risk limit between 1 × 10$^{-4}$ and 1 × 10$^{-6}$ [36].

Following the explanation given by Embiale et al. [27], HQ can be evaluated through the equations

\[ D_{inh} = \frac{C \times InhR \times ED \times EF}{BW \times AT} \]  
\[ D_{ing} = \frac{C \times IngR \times ED \times EF}{BW \times AT} \times 10^6 \]  
\[ D_{der} = \frac{C \times AF \times SA \times ABS \times ED \times EF}{BW \times AT} \times 10^6 \]

In these equations C is the elemental concentration (mg m$^{-3}$); ED is the exposure duration (years); daily doses are represented by $D_{inh}$, $D_{ing}$ and $D_{der}$ for inhalation, ingestion, and dermal absorption (mg kg$^{-1}$ d$^{-1}$), respectively; InhR is the inhalation rate (m$^3$ d$^{-1}$); EF is the exposure frequency (d year$^{-1}$); BW denotes the body weight (kg), AT represents the averaging time (years); IngR is the ingestion rate (mg d$^{-1}$); AF corresponds to the skin adherence factor (mg cm$^{-2}$ d$^{-1}$); ABS symbolizes the dermal absorption factor (dimensionless); SA is the skin surface area of an average man or woman (cm$^2$); RFD is the reference dose corresponding to each intake path (mg kg$^{-1}$ d$^{-1}$), employed to estimate the upper limit for determining if the daily exposure has a low probability of presenting adverse health effects. Cancer risk assessment, is not calculated because there are published values only for Ni [36] among the elements detected in the present study.

The risk assessment due to concentration of elements that may present higher concentrations indoors is mainly focused on the personnel working at the laboratory, evaluating separately for men and women.

In this study, InhR takes different values for women (11.2 m$^{-3}$ d$^{-1}$) and men (15.3 m$^{-3}$ d$^{-1}$) [47]. EF calculation considers the 10 h daily shifts, and only effective working days along one year (218 d); thus EF = 90.8 d yr$^{-1}$. As the laboratory has been operating only recently, a 1 yr value for ED is chosen. The body weight for women is 60 kg and for men is 70 kg [47], while AT = 365 d, to average along one year. Additionally, IngR = 100 mg d$^{-1}$; SA is equal to 2011 cm$^2$ for men and 1694 cm$^2$ for women [27], and ABS = 0.01. Finally, RFD takes different values for each element.

3. Results and discussion

3.1 Mass concentrations

Comparisons were made of mean PM$_{10}$ and PM$_{2.5}$ values inside the laboratory with data measured in outdoor environments by the RAMA CCA and REDMA PED stations (24 h average, along the sampling period). The mean (± standard deviation) for PM$_{10}$ is equal to (7.1 ± 2.5) µg m$^{-3}$ and for PM$_{2.5}$ is (4.2 ± 2.2) µg m$^{-3}$. Indoor values are significantly lower than those outside (Figure 2), as found by means of ANOVA [45,48] ($\alpha = 0.05$); in both cases the value of the probability function F (116 for PM$_{10}$ and 92 for PM$_{2.5}$) is greater than its critical value, $F_C = 4.03$ so the means are different. Moreover, the hypothesis of equal PM$_{2.5}$ means is accepted with ANOVA for gravimetric masses measured outdoors at CCA and at PED ($\alpha = 0.05$, $F = 0.96$, $F_C = 4.03$). Other studies have demonstrated that PM$_{2.5}$ and PM$_{10}$ outdoor concentrations measured at IFUNAM are very similar to those determined at CCA.
and PED stations [43,49]. The World Health Organization (WHO) air quality guidelines (AQG) for particulate matter concentrations (PM$_{10}$ below 50 µg m$^{-3}$, PM$_{2.5}$ 25 µg m$^{-3}$, both 24 h averages) were never exceeded [50]. As there are no standards for indoor pollution in Mexico, and the WHO proposals mention that ‘the WHO AQG for PM can also be applied to the indoor environment . . . ’ [50], the guidelines are used in the present work only as reference parameters.

### 3.2 Elemental analysis

The concentrations of 13 elements in PM$_{10}$ and 12 elements in PM$_{2.5}$ were measured with XRF in samples from the indoor environment. Limits of detection for typical samples on Teflon filters were determined by Mejía-Ponce [40]. Mean elemental concentrations, as determined through XRF, are summarized in Table 1, for both particle sizes.

Most of the elements can be assigned to a crustal origin (Mg, Al, Si, K, Ca, Mn, and Fe), while the rest of them are usually considered anthropogenic (P, S, V, Ni, Cu, and Zn) [51]. The first set of elements have an important contribution for indoors PM$_{10}$ (an average 13% of the total measured mass), and are related to re-suspended dust, probably from the laboratory floor. However, the anthropogenic elements in this fraction contribute to an average of 21% of total gravimetric mass. Similarly, for indoors PM$_{2.5}$, crustal elements contribute with 7%, while anthropogenic elements amount up to 15%. This can be contrasted with the outdoor contributions, where the geogenic elements in PM$_{10}$ had a mean of 15%, against 3% for the same anthropogenic elements. Moreover, for PM$_{2.5}$, the crustal elements average contribution is 7%, and the anthropogenic average is equal to 6%. Therefore, it is apparent that there are very important sources of anthropogenic elements inside the laboratory.

In order to assess which elements had higher concentrations indoors than outdoors of the working area, box-and-whisker plots for the ratio (mass fractions) of the elemental contents to gravimetric mass are presented in Figures 3 and 4, for PM$_{10}$ and PM$_{2.5}$, respectively, both for outdoor and indoor samplings. Graphically, it can be seen that several elements have larger concentrations in the laboratory with regard to the exterior samples, such as S, Ni, Cu, and Zn in PM$_{10}$ and P, S, Ni, Cu, and Zn in PM$_{2.5}$. The use of the Shapiro-Wilk test [45,48] demonstrated that the distributions of the elemental concentrations are not normal, making necessary the use of non-parametric statistical methods. Because of this, a Kruskal-Wallis test, with $a = 0.05$ [45,48] was applied to the elemental concentrations, finding that the means for Mg, Al, Si, K, Ca, V, Mn, and Fe are equal, while the other elements are indeed more abundant in the indoor samples, showing statistically significant higher means. The $p$-values obtained with the Kruskal-Wallis test were smaller than 0.05 (P, PM$_{10}$ 6.7 × 10$^{-6}$; S, PM$_{10}$ 1.6 × 10$^{-5}$, PM$_{2.5}$ 6.2 × 10$^{-5}$; Ni, PM$_{10}$ 2.9 × 10$^{-5}$, PM$_{2.5}$ 5.0 × 10$^{-5}$; Cu, PM$_{10}$ 1.3 × 10$^{-5}$, PM$_{2.5}$ 2.0 × 10$^{-5}$; Zn, PM$_{10}$ 4.7 × 10$^{-5}$, PM$_{2.5}$ 7.2 × 10$^{-5}$), demonstrating that there is an increase of the indoor concentrations of these elements as compared to those measured outdoors. As the laboratory can be assumed as an almost closed environment, due to the requirement of controlling the influence of exterior pollutants, it is necessary to look at possible particulate matter sources inside the laboratory.

### 3.3 Cluster analysis and source identification

As explained above, CA was utilized to find associations among the elements, with the aim to detect common origins of the elements. Figure 5 displays the results for PM$_{10}$ and PM$_{2.5}$, in the form dendrograms. In the first case, Figure 5a shows three different groups: one with Si, Ca, and Fe; a second one with K, Ni,
and Zn, while the third one comprises Al, P, and Cu. Moreover, S is connected to the three groups, a fact that can be explained if this element is common to all of them. This assertion is reasonable, as S presented a large concentration increase indoors. The fine fraction (Figure 5b) exhibits a similar behavior, except that K now is grouped with Al, P, and Cu. The connection of S with all the groups is also observed, with the same plausible justification.

Although it would be desirable to apply other more sophisticated multivariate analytical techniques, such as Factor Analysis (FA) or Principal Component Analysis (PCA), it is necessary first to make other statistical tests to check their feasibility. Hence, it is mandatory to use the Bartlett sphericity test and evaluate the Kaiser-Meyer-Olkin (KMO) index with the elemental concentrations data set [52]. The Stata® statistical package [45] was used for these trials. Concerning the PM$_{10}$ data, the KMO index is equal to 0.715, and for PM$_{2.5}$ it is equal to 0.340. Moreover, Bartlett sphericity test resulted in p values below 0.05, and the determinant of the elemental concentrations matrix is equal to 0. The KMO index must be greater than 0.8 to have reliable FA or PCA results. Therefore, these methods are not applicable to the PM$_{10}$ and PM$_{2.5}$ data sets obtained during this study.

According to the CA results, the first group (Si, Ca, Fe) can be categorized as geogenic aerosol, most probably produced by dust resuspension from the floor or introduced from the exterior, as deduced from their similar concentrations both in PM$_{2.5}$ and PM$_{10}$. Moreover, S may also be present in those particles, as shown in the dendrogram.

It is necessary to identify the possible sources contributing to larger contents of the five elements (P, S, Ni, Cu, and Zn) in the indoor airborne particles, considering the laboratory as an almost closed environment. The most relevant components inside the laboratory are the accelerator itself, vacuum pumps, air conditioning systems and beamlines with their supports. The beamlines are built from wear resistant stainless steel or aluminum, so it is not expected to have an important contribution from this source. Thus, it is

Figure 3. Ratios of elemental to gravimetric mass concentrations (mass fractions) for PM$_{10}$ in samples from (a) the outdoor environment, and (b) the indoor environment (LEMA).
convenient to look at the other three possible contributors, namely, the accelerator, air conditioning and vacuum systems.

A large number of electrostatic accelerators use sulfur hexafluoride (SF₆) as a dielectric gas, due to its good insulating properties. SF₆ is also a strong greenhouse gas [53] with a very long life in the atmosphere [54], but with no reported toxic effects [55]. Nevertheless, SF₆ has many sub-products that are either toxic or corrosive, and chemically very active [56]. Kim et al. [57] and Shin et al. [58] have demonstrated that the dissociation of this gas under electric discharges create the subproducts and other aerosols mentioned above. These processes are not uncommon in electrostatic particle accelerators during their operation. The emitted molecules react with metallic components in the surroundings, creating solid particles emitted to the atmosphere, including Al and Cu compounds, and even there are pure S particles [58]. Kim et al. [57] registered the presence of fine and coarse particles in their experiments. Shin et al. [58] also determined high contents of S in the SF₆ derived particles. Thus, the S and Cu concentrations increase in PM₁₀ and PM₂.₅ can be associated to the dielectric gas. Moreover, the Spearman correlation (at \( p < 0.05 \)) computed for these two elements in PM₁₀ is 0.462, and in PM₂.₅ it is equal to 0.489. Following the criteria described by Taylor [59], this correlation is highly significant, because, due to the number of experimental points, there is a probability below 1% that both variables are not correlated. Another observation is that the Spearman correlation (at \( p < 0.05 \)) between Si and S in PM₁₀ is 0.552, which is also significantly high. This can be understood because S is very often attached to geogenic particles, as explained by Barrera et al. [60], and in agreement with what was stated above. Al possibly does not have a larger impact indoors because of a geogenic contribution.

Some of the reactive compounds derived from SF₆ may escape from inside the accelerator or can be produced outside due to possible SF₆ leaks, and then undergo chemical processes. Accordingly, as a possible SF₆ contribution to the indoor airborne particles was perceived, a search for a potential gas leak was

**Figure 4.** Ratios of elemental to gravimetric mass concentrations (mass fractions) for PM₂.₅ in samples from (a) the outdoor environment, and (b) the indoor environment (LEMA).
performed in the accelerator, using a Dilo (Babenhauen, Germany) model 3–033-R002 SF₆ detector. As predicted, a leak was found in one of the couplings of the accelerator tank, in an estimated amount of 14 g/year, which was then fixed.

Due to the consideration of the laboratory as a closed environment, kept at a constant temperature, the air must be continuously recirculated by air conditioning systems. Ali et al. [61] found that this kind of systems produce an enrichment of the particles by Ni and Zn, especially in fine fractions. Therefore, the Ni and Zn concentration growth in both airborne particle sizes can be explained by this recirculation of geogenic particles, with attachments of Ni and Zn particles. It is noticeably that the Spearman correlation (at \( p < 0.05 \)) between these elements in both particle sizes is significantly high [59], being 0.491 for PM_{10} and 0.684 for PM_{2.5}. Thus, it is very reasonable to conclude that both elements have a common source, explained by the presence of the air conditioning devices and supported by CA results. Again, the inclusion of K in the PM_{10} group is not linked to an enrichment, possibly due to a larger resuspended dust contribution.

Finally, higher contents of P in PM_{2.5} must be justified. Beam lines and scattering chambers in accelerator laboratories must work under high- or ultrahigh-vacuum conditions, frequently obtained with turbo-molecular plus mechanic systems. Both of them need lubricating oils, which emit vapors or particles towards the surrounding air inside the laboratory. In particular, the oil used in this laboratory is Leybold LVO 100 (Leybold, Cologne, Germany). Ruuskanen et al. [62] and Miller et al. [63] carried out elemental analyses of particles produced by mineral lubricating oil, and found, using different methods, important elemental tracers like Si and P. The Spearman correlation (which is significant at \( p < 0.05 \)) for the two elements in PM_{2.5} is equal to 0.674 in the present study, which may support the association of P with the lubricating oil, although this was not reflected in the CA results. Nevertheless, the emissions must also include a large number of organic compounds that were not studied in this work. Therefore, the provenance of P from the pump lubricating oil should be demonstrated with further studies that also include organic emissions.

### 3.4. SEM results

Additionally, only with the aim of exemplifying some of the results, SEM studies were carried on randomly selected samples, among those which were deposited onto polycarbonate filters, as explained above. Figure 6 is associated to a small particle (with maximum length around 3 \( \mu \)m) in a PM_{10} sample. Its spectrum shows the presence of Al, Si, S, Ca, Ba, Fe, and Cu. All these elements are characteristic of a geogenic particle with attached SF₆ subproducts [62], although Ba could not be detected with XRF. Therefore, the elemental analyses with the latter technique and SEM plus EPMA results are compatible. However, a more complete study must include the analysis of other organic compounds, which were not examined in the present work.

To summarize, this study allowed the identification of contributions to particulate matter in the laboratory from the SF₆ dielectric gas, the air conditioning system, and, still to be fully demonstrated, the vacuum pump lubricating oil. It was possible thanks to the complementary application of XRF for elemental analysis, CA, and SEM.

### 3.5. Health risk assessment

It must be recalled that only four elements (S, Ni, Cu, and Zn) showed higher concentrations in PM_{10} and five elements (P, Si, Ni, Cu, and Zn) in PM_{2.5} samples collected indoors; thus, risk assessment was primary focus on these analytes. Nevertheless, there are no RfD values for P and S [64], while it was possible to assess the risk for Fe ingestion.

Table 2 contains several parameters specific to each element, necessary to obtain the HQ values in the present study. From this, Tables 3 and 4 display,
Figure 6. SEM image of a particle detected in a PM$_{10}$ sample, with the X-ray spectra from the area in the rectangle. The particle may be soil-derived dust with SF$_6$ subproducts.

Table 2. Parameters used for risk assessment, indoor PM$_{10}$ elemental concentrations [28,32].

| Element | $R_{ID}$ | IUR | SF | G |
|---------|----------|-----|----|---|
|         | Inhalation | Ingestion | Absorption |   |
| S       | NA       | NA   | NA  | NA |
| Fe      | NA       | 0.7  | NA  | NA |
| Ni      | 0.00005  | 0.05 | 0.24 | 0.00384  |
| Cu      | 0.04     | 0.4  | 1   | NA |
| Zn      | 0.04     | 0.4  | 1   | NA |

*Not available.

respectively, the PM$_{10}$ and PM$_{2.5}$ risk assessment results for each process (inhalation, ingestion, and dermal absorption) due to the elements with higher concentrations indoors. It must be recalled that, according to section 2.7, these evaluations correspond to a one-year period, for 10-hour shifts. From the data in Tables 3 and 4, and following the US EPA criteria [36] and arguments given by Embiale et al. [27], none of the elements represent a health risk, as the HQ values are

Table 3. Risk assessment results for inhalation, ingestion and dermal exposition to PM$_{10}$ at the LEMA.

| Element | $C$ | $D_{inh}$ | $HQ$ |
|---------|-----|-----------|------|
|         | mg/m$^3$ | mg kg$^{-1}$ d$^{-1}$ |    |
|         | Men | Women | Men | Women | Men | Women | Men | Women |
| S       | 1.03 $\times$ 10$^{-3}$ | 1.22 $\times$ 10$^{-7}$ | 1.06 $\times$ 10$^{-7}$ | 1.15 $\times$ 10$^{-1}$ | 1.34 $\times$ 10$^{-1}$ | 4.27 $\times$ 10$^{-7}$ | 3.15 $\times$ 10$^{-1}$ | 3.61 $\times$ 10$^{-1}$ |
| Fe      | 2.30 $\times$ 10$^{-4}$ | 2.72 $\times$ 10$^{-8}$ | 2.36 $\times$ 10$^{-8}$ | 2.99 $\times$ 10$^{-2}$ | 3.66 $\times$ 10$^{-2}$ | 4.27 $\times$ 10$^{-2}$ | 3.61 $\times$ 10$^{-2}$ | 4.27 $\times$ 10$^{-2}$ |
| Ni      | 1.19 $\times$ 10$^{-4}$ | 1.41 $\times$ 10$^{-8}$ | 1.22 $\times$ 10$^{-8}$ | 1.55 $\times$ 10$^{-2}$ | 2.65 $\times$ 10$^{-2}$ | 3.09 $\times$ 10$^{-2}$ | 3.09 $\times$ 10$^{-2}$ | 3.09 $\times$ 10$^{-2}$ |
| Cu      | 1.60 $\times$ 10$^{-5}$ | 1.90 $\times$ 10$^{-9}$ | 1.64 $\times$ 10$^{-9}$ | 4.74 $\times$ 10$^{-8}$ | 4.11 $\times$ 10$^{-8}$ | 4.11 $\times$ 10$^{-8}$ | 4.11 $\times$ 10$^{-8}$ | 4.11 $\times$ 10$^{-8}$ |
| Zn      | 1.42 $\times$ 10$^{-4}$ | 1.68 $\times$ 10$^{-8}$ | 1.46 $\times$ 10$^{-8}$ | 4.20 $\times$ 10$^{-7}$ | 3.65 $\times$ 10$^{-7}$ | 3.65 $\times$ 10$^{-7}$ | 3.65 $\times$ 10$^{-7}$ | 3.65 $\times$ 10$^{-7}$ |
smaller than 1 in every case. It is apparent that hazard quotients values due to inhalation of PM$_{2.5}$ are lower than PM$_{10}$ HQ. This fact is reasonable, as the concentrations of the elements found in PM$_{2.5}$ are smaller than those found in PM$_{10}$, because the fine fraction is a component of the latter and, consequently, the same can be said about the elements under study. Despite PM$_{2.5}$ can penetrate deeper in the respiratory tract, the fraction of total PM$_{2.5}$ that can be deposited in the lungs of an adult, where there may be a higher cancer risk, is around 30%, while that in the upper respiratory tract amounts to nearly 40%, according to an indoor environment study published by Madureira et al. [65]. Therefore, the elemental concentrations measured in PM$_{2.5}$ may actually represent the upper limit for HQ in Table 3, for estimations of adverse health effects in the lungs. It would require a different study to determine the effect of the elements deposited in the other regions of the respiratory tract to assess the risk caused by the accumulation of PM$_{2.5}$. Finally, it is not expected that the remaining elements (Al, P, Si, K, Ca), mostly associated to a crustal origin, represent a high risk. It must be mentioned that no information is available for the RfD of these elements.

### 4. Conclusions

The present work represents the first published investigation about the air quality in a small particle accelerator laboratory. Indoors gravimetric mass and elemental concentrations in PM$_{10}$ and PM$_{2.5}$ were determined at LEMA, showing that, although mass concentrations are lower than outdoors, several anthropogenic elements show significantly higher contents, in particular S. The use of Cluster Analysis allowed the recognition of at least four sources. It was shown that there was an important contribution of geogenic sources, as well as emissions from the SF$_6$ dielectric gas of the accelerator itself (with probable sub-products). Also, the effects of air conditioning devices, recirculating the particles, is observed through Ni and Zn. Finally, the increase in the P concentrations in PM$_{2.5}$ due to the mineral oil used in the vacuum pumps requires further studies to be confirmed. The hazard quotients due to inhalation, ingestion, and dermal absorption of PM$_{2.5}$ and PM$_{10}$ did not exceed the value recommended by the US-EPA (HQ < 1), so these airborne particles do not represent a threat to the health of the personnel. This work demonstrates the need to look more carefully at the air quality and possible effects on the health of personnel working in this kind of laboratories, due to the high number of low-energy accelerators installed around the world. More investigation about the presence of organic compounds is still necessary.

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Appendix

The measurement of the concentrations of each element with XRF must include the evaluation of the corresponding uncertainty. In particular, the concentration $C_Z$ of element $Z$ is given by:

$$C_Z = \frac{N_{X,Z} n(Z)^2}{k(Z) T Q_n t}$$

(A.1)

Here, $N_{X,Z}$ is the number of X-ray photons emitted by element $Z$ and registered by the detector, $D$ is the diameter of the particle deposit on the filter, $k(Z)$ is the response function of the X-ray detection system, $T$ is the irradiation time used to obtain the spectrum for this sample, $Q_n$ is the actual air flow in the sampling device (corrected for calibration, as well as local temperature and pressure), and $t$ is the time required to collect the particulate matter sample. The application of Eq. (10) from JCGM [66] to Eq. (A1) results in an equation for the evaluation of the combined uncertainty $u_C(C_Z)$ for this elemental concentration:

$$u^2_C(C_Z) = C_Z^2 \left[ \frac{u^2(N_{X,Z})}{N_{X,Z}^2} + \frac{4 u^2(D)}{D^2} + \frac{u^2(k(Z))}{(k(Z))^2} + \frac{u^2(T)}{T^2} + \frac{u^2(Q_n)}{Q_n^2} \right] + \frac{u^2(t)}{t^2}.$$  

(A2)

where $u(X)$ represents the combined uncertainty for quantity $X$. As explained in JCGM [66], this procedure is valid when the quantities involved in the determination of $C_Z$ are not correlated, which is actually the case.

The response function of the detection system is obtained from:

$$k(Z) = \frac{N_{X,\text{Std}}}{T_{\text{Std}}}.$$  

(A3)

equation in which $N_{X,\text{Std}}$ is the number of X-ray photons in the peak of element $Z$, registered by the detector and emitted by a thin film standard with certified thickness $t$, with a 5% uncertainty, and $T_{\text{Std}}$ is the time required to collect the spectrum. Thus:

$$u^2(k(Z)) = k^2(Z) \left[ \frac{u^2(N_{X,\text{Std}})}{N_{X,\text{Std}}^2} + \frac{u^2(t)}{t^2} + \frac{u^2(T_{\text{Std}})}{T_{\text{Std}}^2} \right]$$  

(A4)

The uncertainty of the particulate matter sample collection time is $u(t) = 0.1 \ h = 6 \ min$, that of the filter diameter is $0.1 \ cm$, $u(N_{X,Z}) = N_{X,Z}^{1/2}$, $u(N_{X,\text{Std}}) = N_{X,\text{Std}}^{1/2}$ [67], while the uncertainties in the spectra collection time are considered negligible, as they are fixed with the detection system electronics. Details for the determination of the uncertainty in the actual air flow $Q_n$ are better explained in reference [68].