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Research Paper

An analysis of vehicular exhaust derived nanoparticles and historical Belgium fortress building interfaces

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ABSTRACT

Air pollution monitoring is one of the most important features in contamination risk management. This is because many of the compounds contained within air pollution present a serious risk both for the preservation of open air cultural heritage and for human health. New particle formation is a major contributor to urban pollution, but how it occurs in cities is often puzzling. As more and more people enjoy an increased quality of life through outdoor activity, managing outdoor air quality is vital. This study presents the application of a low-cost system for monitoring the current level of road traffic passengers' exposure to particulate air contamination. The global rise in tourism also leads to apprehension about its probable destructive influence on various aspects of global preservation. One of the major risks encountered by tourists, stemming from modes of transport, are nanoparticles (NPs) ($\leq$100 nm) and ultra-fine particles (UFPs) (100–1000 nm) consisting of potentially hazardous elements (PHEs). This study examines Steen Castle, a medieval fortress located in Antwerp, Belgium. Significant NPs with PHEs, were found in the air sampled in this area. The self-made passive sampler (LSPS) described in this study, consisting of retainers specially designed for advanced microscopic analysis, is used for the first time as a simple way to characterize the surrounding atmospheric contamination caused by NPs and UFPs, without the need of other commonly employed more expensive particulate focused active samplers such as cascade impactors. This study aims to assess the result of the utilization of a low-cost, LSPS, to determine outdoor NPs and UFPs in a Belgian urban (Steen Castle) and rural area (Fort van Schoten). This work is the first to detail the usefulness of LSPS for the evaluation of Belgium's outdoor air for NPs and UFPs, which contain PHEs.

1. Introduction

Global scientific study has focused on researching forms of contamination in the localized atmosphere, water and soil, which can potentially contain high levels of contamination (Dotto et al., 2011, 2012, Dotto et al., 2015a, 2015b, 2016; Vieira et al., 2014; Moura et al., 2015; Souza et al., 2017; Thue et al., 2017; Umpierres et al., 2017, 2018; Peres et al., 2018; Rodrigues et al., 2018; Sajjadi et al., 2018; Li et al., 2020). These contaminants are commonly derived from sources that vary as widely as motor vehicle exhaust, construction compounds, dust, physical erosion, and hazardous biological aerosols, in areas commonly frequented by tourists (Agudelo-Castañeda et al., 2016; Rojas et al., 2019; Li et al., 2020). New particle generation in cities is especially important, in part because levels of air pollution in cities constitute a public health crisis (Agudelo-Castañeda et al., 2017), but also because the regional climate forcing associated with mega-city urban haze can be significant. However, new particle formation in highly polluted cities is often perplexing, as the apparent particle growth rates are only modestly greater (roughly by a factor of three) than growth rates in remote areas; whereas the vapor condensation sink (as compared to background particles) is up to two orders of magnitude larger. This implies a very low survival probability in the 'valley of death,' where particles with diameters of 10 nm or less have high Brownian diffusivities and will be lost by coagulation scavenging unless they grow rapidly (McMurry et al., 2005). Such transients will be difficult to identify in heterogeneous urban environments, yet have the potential to explain the puzzling observations of new particle formation in highly polluted cities.

In Europe's cities, air contamination is an important environmental

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and human health risk factor (EEA, 2018). Maintaining adequate air quality, while ensuring the required level of mobility, is one of the major challenges facing the region's legislators. High levels of road congestion reduce the usefulness of shared, public space, increases travel time, and causes excessive emission of air pollutants. The experience of road congestion is, unfortunately, becoming increasingly common. Additionally, tourism, according to Pulido-fernández et al. (2019) needs to be regulated through public policies that minimize the impacts of particulate matter derived from vehicle exhaust on the environment. The burning of fossil fuels in internal combustion engines results in the emission of carbon and other compounds which are likely to impact tourist diversity in both the short and long term (Zhang et al., 2019). Furthermore, these compounds have the potential to compromise the physical structure of historical buildings by interacting with the materials from which they are constructed and/or allowing for accretions on their surfaces according to Arjonilla et al. (2018), Pranjić et al. (2018) and Arjonilla et al. (2019). Additionally, atmospheric contaminants can also be found in locations with little to no vehicle exhaust (Madureira-carvalho et al., 2018). According to Pinheiro (2017), one solution to this problem is the incorporation of smart city design (urban mobility through different connections) and an increase in green space. This not only preserves and enhances tourism, an essential source of income for the local population and economy; it also had the added impact of helping to conserve irreplaceable sites of historical heritage (Brtnický et al., 2020).

Old buildings with historic value also contain an indoor atmosphere in need of protection, as tourists enter the buildings and do not simply remain outside. Tourist visitors to enclosed areas with poor indoor air quality represent a potentially susceptible population with very real potential respiratory health consequences (Azam et al., 2018; Pranjić et al., 2018; Zhang et al., 2019). Studies of particulate matter (PM) containing nanoparticles (NPs) and ultra-fine particles (UFPs) have also shown the impact on children to respirable ecological pollutants, principally less hazardous organic and inorganic compounds (Schneider et al., 2016; Rojas et al., 2019).

Increased localized levels of pollutants in the atmosphere are often directly attributable to increased tourism in sparsely populated zones. This is principally driven by both the construction of new infrastructure and by vehicular and air transport (Davenport and Davenport, 2006; Massas et al., 2016; Ciarkowska, 2018; Alsamhi et al., 2019). Evidence highlighting this is crucial for developing and implementing effective strategies to mitigate air pollution. When the specific probability function of a particular air pollutant is identified, it is easier to statistically predict the required emission reduction, the mean concentration, the frequency of exceedance of the air quality standard, as well as the return period. It is also efficient in order to investigate the similarities and differences among the types and concentrations of air contaminants of diverse global areas. On the other hand, sustainable urban development requires reducing inhabitants' exposure to air pollution in the vicinity of road infrastructure (Silva et al., 2020). Knowledge of the impact of road traffic on air quality is the basis for effective action in this area. Total emission balance was our preferred indicator for assessing the overall level of impact. However, this approach does not make it possible to observe changes occurring in relatively short time intervals, such as 1 h. Continuous monitoring of air pollution seemed more useful for verifying the effectiveness of the urban mobility scenarios being implemented. In practice, however, the options for monitoring exposure to air pollution in the vicinity of road infrastructure using a traditional air quality monitoring network are limited. A relatively rare and expensive network of stationary measurement sensors does not provide sufficient spatial resolution to observe emission episodes related to traffic distribution. As a consequence, the effects of exposure to pollution hot spots remain poorly investigated. It can be reasonably inferred that low-cost sensors will be widely used in the near future to examine this particular issue. Air quality monitoring using a network of such sensors will provide the necessary data, which, in combination with predictive models, will be a useful tool for developing strategies to prevent conditions that lead to high levels of emissions (Rojas et al., 2019). It is believed that the application of low-cost samplers has already changed the paradigm of air pollution monitoring, and application of these technologies is set to grow (Schneider et al., 2016). In addition to the price, the undoubted advantages of low-cost samplers include small dimensions, low demand for power supply, and the ability to obtain information in close to real-time (Silva et al., 2020). These features enable the construction of multi-sampler networks carrying out direct measurements in the area of impact of traffic-related emissions.

The main motivation of the present study is to distinguish whether vehicular traffic related activities (principally, vehicle exhaust) increase NPs + PHEs and to determine the influence of that exhaust on levels of PM contamination sampled in Steen Castle, Belgium. Outdoor samples for the measurement of NP and UFP were collected under realistic urban and rural conditions. This study represents an indispensable phase in the development of effective air quality policies that limit the amount of pollution the general public and tourists are exposed to on a routine basis in both a rural and urban area in Belgium popular with tourists.

2. Materials and methods

2.1. Study area

The present study evaluates the NPs and UFPs collected from sampling sites around Steen Castle (a medieval fortress, Fig. 1) and a rural area (Fort van Schoten). Steen Castle is the oldest building in Antwerp, Belgium, part of a previous castle on the right bank of the Scheldt River. The castle was built at the beginning of the 13th century. In the 16th century it was thoroughly rebuilt under Charles V. In the 19th century most of the complex was demolished in an effort to straighten the castle's quays and lessen their impact on the river. Antwerp is situated on the Scheldt River, about 55 miles (88 km) from the North Sea. The Scheldt, together with the Meuse and the Rhine, form the biggest estuary in Western Europe, and Antwerp is an essential part of an enormous harbor complex, one of the greatest in the world. The harbor installations of Antwerp grew significantly following World War II. For many years this expansion took place on the right bank of the Scheldt only, but beginning in the 1970s there was increased development on the left bank as well.

The control/blank zone area used in this study was Fort van Schoten (Fig. 1). This region is highly wooded, devoid of large industry and high vehicular traffic.

2.2. Samples compilation and analytical method

Forty-seven samples were collected in 2017 and 2020 in an effort to evaluate both the PHEs in proportion to the NPs and their overall levels of occurrence within the area. The low-cost, self-made passive sampler (LSPS), previously reported by Silva et al. (2020), was mounted in the sampling areas (Fig. 1) and was utilized to directly accumulate PM of multiple sizes and shapes. For this study, a Cu-grid of HR-TEM at LSPS was also added for the analysis of NPs. Such a procedure does not require sample preparation to be analyzed by advanced microscopy (AM), Raman Spectroscopy (RS), and X-ray powder diffraction (XRD). This results in more realistic results, which do not alter the nature of the sampled particles. This inert LSPS consists of a PVC tube with one interior pin stub covered with C-tape (Silva et al., 2020).

The solid fraction was analyzed with X-ray Bruker diffractometer (model D8 DISCOVER) with NAP-LOCK X-ray optics to examine mineralogy and amorphous phases' occurrence (Ramos et al., 2017). Working conditions were as follows: slit fixed at 12 mm, Cu Kα monochromatic radiation, current 20 mA at 40 kV. Samples were scanned at a speed of 0.3° 2θ/min (5°–65°). The UNPs samples with mixed compounds were studied by X-ray diffraction (Gasparotto et al., 2018) and advanced electron-beam (high-resolution transmission electron microscope, HR-TEM, 200 kV) prepared with a FE cathode and an energy omega filter

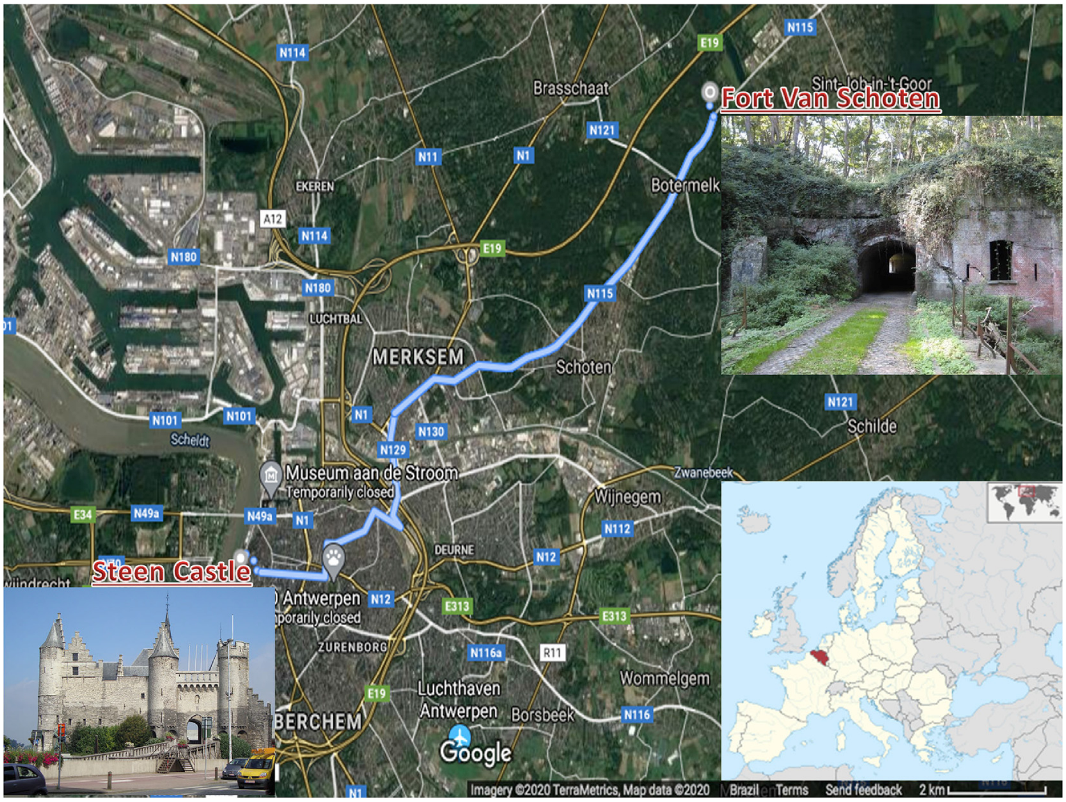

Fig. 1. Location of study areas (rural and industrial).

for high accuracy of the assembly and atomic arrangement, fast Fourier transform (FFT), microbeam diffraction (MBD), selected area electron diffraction (SAED), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments INCA 4.09 software; Hovington et al., 2016). The chemical components with high atomic numbers appear in the brightest areas of the identified image and those with low atomic numbers in the dark-field areas. The AM/EDS reveal that the PM has slightly diverse geochemical conformation (Rodriguez-Iruretagoiena et al., 2015). Before microscopic analysis, the specimen holder was cleaned with an advanced plasma system (Gatan Model 950) to minimize contamination. Even so, a blank was analyzed at the same time as the samples in order to ensure that the samples do not contain impurities from the specimen holder. A field emission scanning electron microscope (SEM) model sigma 300 VP (Carl Zeiss, England) with field emission filament (FEG-Fiels Emission Gun) of the Schotky type (tungsten filament covered with zirconium oxide), equipped with a Gemini column (Zeiss, England) was utilized. The images were obtained using the secondary detector (SE2) in high vacuum mode (1×10^{-9} bar), energy of 1 KV, working distance of 5 mm, opening of 20 μm and magnifications (1000×, 2500× and 5000×). And the EDS spectra were used the EDS X-ray detector (model Quantax 200-Z10, Bruker, Germany) equipped with a 10 mm^2 quartz window and ESPRIT software. The EDS were obtained using the secondary detector (SE2) in the variable pressure mode, which consists of the insertion of N_2 gas in the sample compartment, allowing the variation of the partial pressure between 1 Pa and 133 Pa ($1\ \text{Pa} = 1 \times 10^{-5}$ bar), working distance 8.5 mm, energy of 20 kV and an opening of 60 μm.

3. Results and discussion

Numerous toxicological investigations have shown vehicular traffic-related organic NPs and ultra-fine particles, particularly diesel, to be linked with adverse human health including pulmonary inflammation, asthma exacerbation, and lung infections (Niu et al., 2020). This is consistent with the findings of this study. McDonald et al. (2004) reported that lung toxicities could be governed by contributions from both high and normal emitting vehicles. Internal combustion engines emit large amounts of PAHs that partition between gas and particle phases, while diesel exhaust contains higher amounts of volatile and semi-volatile PAHs than that of gasoline vehicles (Zhu et al., 2017). Rapid growth may contribute to the often puzzling survival of newly formed particles in mega-cities, where particles form at rates consistent with sulfuric-acid–base nucleation and appear to grow at typical rates (roughly 10 nm h^{-1}) in the presence of extremely high condensation sinks that seemingly should scavenge all of the tiny nucleated particles (Wang et al., 2020). The persistence of newly formed clusters depends on the ratio of the condensation sink (the rate at which vapor and clusters are scavenged by pre-existing particles) to the growth rate of the clusters themselves. In the real world, both of these quantities depend on particle-size distribution. The condensation sink can be derived directly from the particle-size distribution; however, the growth rate is commonly determined by monitoring how clusters grow over time, typically in the size range between 1 nm and 10 nm. This method assumes that the environmental factors that affect cluster growth are uniform throughout a given region, and it has worked well in describing particle-growth behavior in rural environments. It has, however, failed to explain particle growth in cities (Kulmala et al., 2017).

In recent years the focal point of several investigators was concentrated primarily on the impact of gaseous contaminants on stone or mortar deteriorations, especially that of S-dioxide (Ozga et al., 2009). Several regions of Europe have experienced reductions in the concentration of SO_2 while concurrently seeing an extensive rise in the levels of O_3, NOx and NPs as a result of a large rise in vehicles of all types on roadways (Valotto et al., 2018). Aerosols that result from internal combustion engines are also recognized as a main cause of atmospheric contamination in urban atmospheres. Samples collected in the studied area revealed NPs and ultra-fine particles; these include minerals, mineraloids, organometalic compounds, carbonaceous matter, and elemental elements. In general, the NPs and UFPs detected in this work were of multiple sizes, morphologies, geochemical compositions and reactivity. By separating the particles into condensed water and precipitate particles it was possible to obtain more clarifying results, especially regarding their reactivity, and therefore possible effects on construction materials and NPs speciation. The air quality in the immediate vicinity of the road is worth comparing with background levels of NPs and UFPs. This comparison leads to the conclusion that traffic has a significant negative impact on air quality.

The gathered samples have been worked extensively by XRD and advanced microscopies (Table 1 and Supplementary Fig. 1). The main minerals detected in this matrix were: barite, brushite, calcite, dolomite, ferrohexahydrite, gypsum, hematite, quartz, kaolinite, illite, magnetite, goethite, siderite, mullite, magnetite and rutile. These are minerals almost always derived from soils, residues of construction material, and/or road dust material. Some minerals such as magnetite and mullite have been reported by other studies to be formed in internal combustion engines and emitted in vehicle exhaust (Bardelli et al., 2011; Hovington et al., 2016; Zanoletti et al., 2020). The authors assume corroboration with the previously published studies, since analyzed samples from the rural area did not detect such minerals, whereas samples collected from the urban area did (Table 1).

Only 5% of the 172 particles collected in the rural area were carbonaceous, probably from combustion of buses and tractors used in the region. While in the urban area under study 89% of the studied areas were carbonaceous, demonstrating the impact of vehicular traffic on the heritage site under study. We infer that air quality in the urban area under study is impacted not only by refineries and industry, but also by intense levels of vehicular traffic. This is demonstrated by an excess of black crusts in Steen Castle itself. In the rural area studied, no black crusts were detected, with biodegradation being the main reason.

The morphology of urban UFPs and NPs linked to UFPs (Fig. 2A and B) indicate that human activities add many particles to the condensate geochemistry. The applied sampling in the urban area shows material containing particles are very similar to the combustion of fuels such as diesel, which is common in the urban region, and are the ones that contributed the largest amount of UFPs in the building under study during the time of this study.

Several particles with macro, micro and nanopore sizes were easily detected by FE-SEM and HR-TEM. Fig. 2 illustrates the typical morphology of UFPs and micrometrics particles, showing that many are porous and that they contain even smaller particles in their pores. In general, pore size can be essentially considered total particulate size, encompassing mesopores and macropores (Zanoletti et al., 2020); though, an officially recognized description of the basis of pore size dimensions cannot be found in previous works (Zdravkov et al., 2007). Our study defined micropores as size $r > 50–100$ μm, and mesopores as size $r < 101–1000$ μm. Detected porous ultra-fine particles represents a high risk to indoor air quality as they serve as NPs stores, which can become detached and enter the bloodstream when inhaled. A similar risk exists with microparticles containing agglomeration of NPs and UFPs on their surface. In general, larger particles contain only elements such as: Al, Si, Fe, K, Mg, Na and others that are not considered highly toxic. While particles smaller than 500 nm contain other elements such as: Cd, Cr, Pb, Ti and Zn that present a greater health risk when absorbed into the bloodstream. The studied historical castle was situated in close proximity to active roads, which increases the level of vehicular transportation-connected atmospheric contaminants in the building's air. This contamination has the potential to produce a variety of negative health impacts, leading to reduced life spans (Silva et al., 2020). The occurrence of certain NPs + PHEs in high proportion is a matter of great concern. This work recognizes the health risks associated with inhalation of NPs in urban locations. Therefore, to reduce overall exposure to NPs and UFPs, both in urban and rural settings, effective regulatory and mitigation practices should be developed, implemented, and enforced. Particle preparation by FIB-SEM permits non-destructive pores size, geochemical, and morphology analysis. HR-TEM, and EDS analysis permitted us to highlight the NPs' chemistry and circulation in the porous compounds. Titanium-Fe-containing atmospheric PM presents a significant health risk, due to its cytotoxicity and the oxidative infection stress it causes in the cells of numerous organs. While small concentrations are difficult to detect, pores with sizes smaller than 100 nm can be underscored. The real reasons for the association between nanominerals and porous particles can be via nucleation, reactivity and/or simple agglomeration by dry deposition during atmospheric exposure. However our current analytical methodologies do not allow us to outline precise and/or exact reasons. Similar results were previously reported by several studies (Bardelli et al., 2011; Hovington et al., 2016; Cobo-Golpe et al., 2020; Zanoletti et al., 2020). It is likely that the occurrence of Fe-Ti-NPs in the internal pore assembly can be credited to the incidence of associated pores.

The agglomeration of nanominerals and NPs in fibrous material is illustrated by Figs. 3–5. This was noticed only in samples taken from the urban area. The detected fibers from urban samples by LSPS (Fig. 3) have a high deposition capacity and agglomeration of NPs, so the risk to historical buildings and human health is even greater since such NPs can separate from the fibers and move throughout the body of children exposed to such particles through respiration. UFPs and NPs agglomerated in fibrous compounds exhibit a soil and/or construction material composition, almost always containing: Fe, Al, Si, Na, Mg, S, K, Ca, O, and C as illustrated by general EDS graphic (Fig. 3). No fibers were detected in samples collected in the rural area. Using FE-SEM it was possible to detect that even naturally occurring minerals may contain anthropogenic NPs, this is due to nucleation, dry deposition, and atmospheric geochemical reactions. Reflecting on the main probable impact upon historic building conservation and children's health via airborne NPs, this work contributes to the overall detail of geo-mobility and particle dispersal in black crusts. Microparticles and ultra-fine particles of Ca-sulphate were composed of euhedral minerals approximately 1.5 μm thick and up to 320 μm long which display crushed morphologies changing from bladed to platy conducts. Gypsum detection agrees with other cultural heritage monuments' observation extracted by FE-SEM/EDS (Oliveira et al., 2019, 2020; Silva et al., 2020). The occurrence of Ca-sulfates adds new ions to the historical building material conformation, which may lead to the formation of new compounds changing the original mechanical properties of the compound. Furthermore, due to the porous nature of the mortars, water dissolved ions can penetrate and flow through them. The mineral and amorphous salts can crystallize when water is evaporated and the activity of the ions exceeds the saturation one, but also when the relative humidity in the atmosphere that surrounds the material is lower than the equilibrium saturated solution of that salt. Therefore, in a porous system, accumulated salts will crystallize and dissolve depending on the relative humidity of the environment. These continuous sequences are able to devastate the mortars

Table 1
Minerals of solid particles by XRD, FE-SEM and HR-TEM.

Mineral	Rural Area	Urban Area
Barite, $BaSO_4$		X
Brushite, $CaHPO_4 \cdot 2H_2O$	X	X
Calcite, $CaCO_3$	X	X
Dolomite, $CaMg(CO_3)_2$		X
Ferrohexahydrite, $FeSO_4 \cdot 6H_2O$		X
Goethite, $Fe(OH)_3$		X
Gypsum, $Ca[SO_4] \cdot 2H_2O$	X	X
Hematite, Fe_2O_3	X	X
Illite, $K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(OH)_4$	X	X
Kaolilite, $Al_2Si_2O_5(OH)_4$	X	X
Magnetite, Fe_3O_4		X
Mullite, $3Al_2O_3 \cdot 2SiO_2$		X
Quartz, SiO_2	X	X
Rutile, TiO_2	X	X
Siderite, $FeCO_3$		X

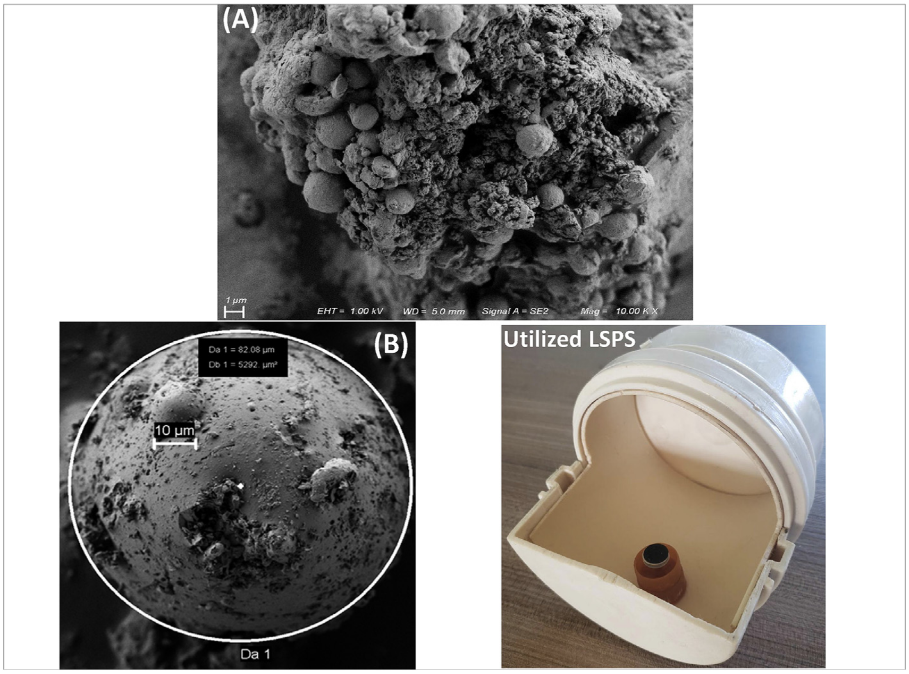

Fig. 2. General UFPs FE-SEM view of self-made passive sampler utilized in this study.

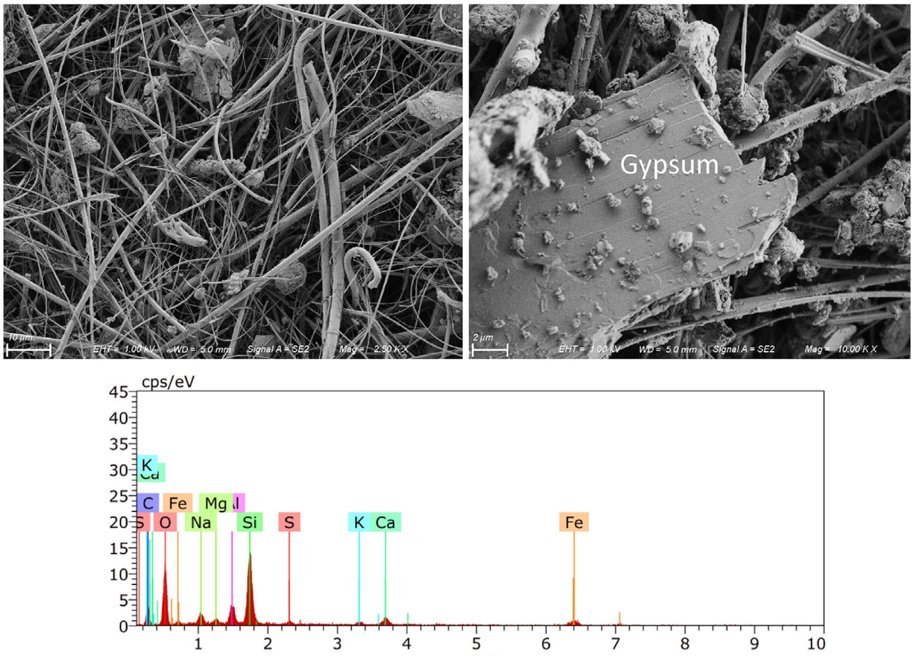

Fig. 3. FE-SEM images of fibrous materials, and a general EDS of deposited UFPs.

mechanically because of the pressures produced during the crystallization process due to the growth of the crystals and to their hydration development.

The concentration of compounds contained within vehicle exhaust are determined by the vehicle's technology, type of fuel burned, lubricant oils used, as well as the driving patterns of the driver (Rivas et al., 2020). With the rapid increase in traffic in the City of Antwerp, and an overall intensification in localized anthropogenic activity, NPs + PHEs pollution can be forecast to increase rapidly in the coming years. This study shows an association among pollution and the secondary creation of many carbonaceous mixtures and combustion byproducts in the area studied. Of the 481 carbonaceous urban NPs detected by HR-TEM and FE-SEM, only 139 did not contain impurities such as: Al, Si, Ca, and other major elements (e.g. Fig. 3). That is, they were composed only of: C, N, S, O, N, and trace elements. Most organic urban NPs were detected in the general vehicular area, and contained PHEs such as: Cr, V, Ni, Sb, Zn, Cr, Fe, and others (see Fig. 4) that are typically derived from combining oil products and road dust. Therefore, the association of carbonaceous NPs with these elements shows that the excess traffic in this area is the main source of organic anthropogenic NPs.

The particle size distribution of the 481 particles is reported as follows. 16% were particles larger than 500 nm, and always presented

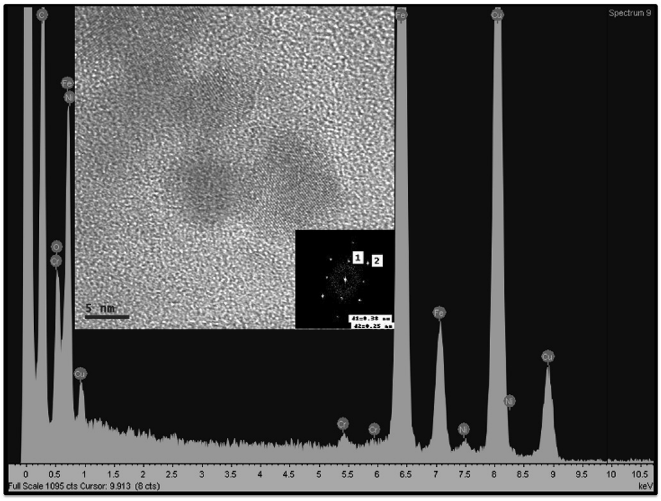

Fig. 4. HR-TEM image of organometalic aggregates of amorphous and crystalline nanophases containing Cr and Ni (EDS spectrum containing Cu from grid). FFT image of nanocrystals.

themselves as clusters of amorphous phases containing minerals and organometalic forms; 29% were particles agglomerated between 100 nm and 500 nm, and in most cases they were in isolated phases (fibers, minerals and amorphous compounds) containing smaller agglomerates between 5 nm and 57 nm deposited on the surface, which were almost always composed of PHEs; 31% were carbonaceous particles agglomerated between 50 nm and 100 nm, which hardly contained any PHEs; The remainder of the particles were smaller than 50 nm and could be agglomerates or isolated phases of minerals, carbonaceous matter, organometalic and several complexes phases. Niu et al. (2020) ranked nanoparticulate matter toxicity from fuel combustion, finding that diesel fuel was more toxic than gasoline. Increases in mRNA and protein expression of pro-inflammatory mediators were also observed in human lower respiratory tract cells after exposures to PM2.5 diesel exhaust (Salvi et al., 2000). Further experiments on genotoxicity and related pathways are required to investigate the underlying mechanisms of PM2.5 from both diesel and non-diesel fueled vehicles with respect to human respiratory system damage. In this context the considerable increase in the tourism sector, with increased emissions from air and sea transport, was responsible for the organic NPs detected in this study. Diesel-fueled vehicles are the major contributor to toxic NP generation due to the higher toxicity responses during morning rush hours with predominance of diesel vehicles. Decreasing the use of diesel fuel can effectively reduce the toxic effects to the respiratory system. In view of this reality, it is recommended that plans for improving air quality should be based on integrated strategies focusing on urban emissions and specific critical points.

Less bright organometallic UFPs and NPs correspond in most of the cases to iron and carbon particles. In some of detected UFPs and NPs, iron is present with other elements such as Cd, Cl, Cu, Cr, As, Pb, Mn, Sb and Sn, which according to the low intensity of the signals, are present in a lower extent. All the organometallic detected particulate matter has a diameter below 1000 nm. Several non-crystalline compounds, or amorphous phases, also occurred, probably because ground dust (which can form suspended dust) and air dust may contain construction material (Fig. 5). Recent authors (Bardelli et al., 2011) studied that the iron species in road dust, sampled from the "Traforo del San Bernando" tunnel, was dominated by Fe-oxides and Fe-chlorous phases, credited to vehicle exhaust and salt. Furthermore, in Brazil and China, Rojas et al. (2019) and Zhang et al. (2019) described that the high concentrations of Fe-hydr/oxides were derived from metallurgical causes. Iron UFPs and NPs were the more widely dispersed on the retainers. Iron containing NPs can be produced as a result of diverse engineering and metallurgical activities, shipping, combustion of fuels, tire and break wear, and other traffic emissions (if Fe-compounds were added as catalysts in engines) (Oliveira et al., 2020). Iron NPs are also sourced from the re-suspension of crustal material (Silva et al., 2020). The areas where the LSPSs were fixed are in a highly industrialized zone with heavy traffic activity. The LSPSs were just above a very busy road. Additionally, the authors wish to highlight the enormously comparable detection levels of aluminum and silicon, which may be due, yet again, to the occurrence of alumino-silicate accumulations. These compounds exist in the dust of the

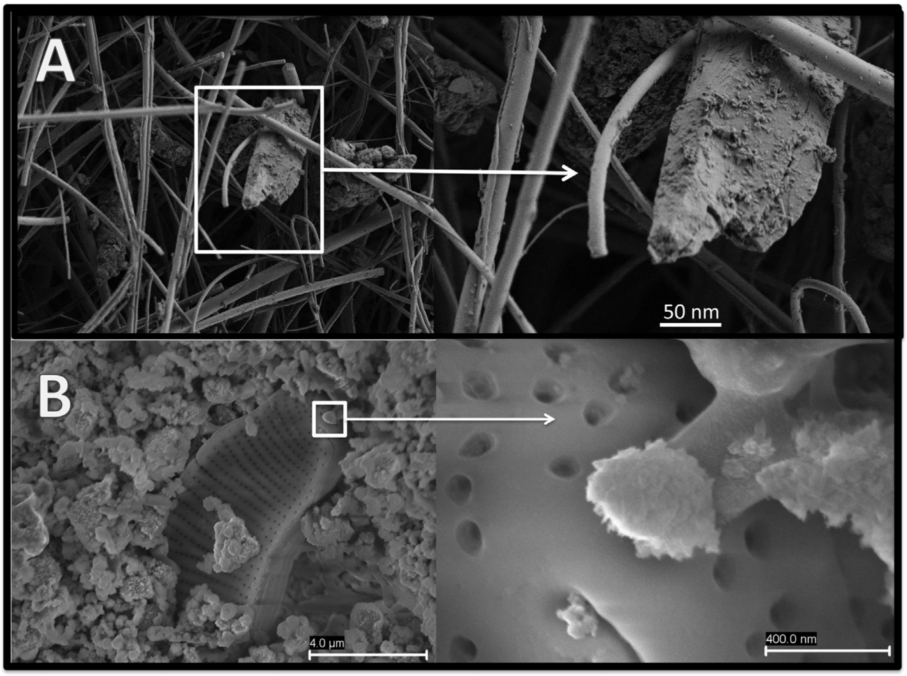

Fig. 5. Images of non-crystalline phases, where (A) fibrous compounds contain several agglomerated organic nanoparticles, and (B) bioaerosol from the rural area studied.

atmosphere but also in the fine-grained sediments deposited in the nearby beach sands.

The results demonstrate the applicability of LSPS, combined with advanced microscopies and XRD, to understand the impacts on historical building construction material exposed to NPs and PHEs. However, the analysis presented in this study was developed over a short time scale and does not allow us to determine the robustness of the LSPS system to this study over time.

4. Conclusions

This study outlines a novel, original, inexpensive, and capable method to sample and analyse outdoor air quality and pollution levels near historical cultural heritage structures. One's exposure to contaminated air depends on the amount of time that an individual spends in specific conditions, characterized by the level of atmospheric contamination in that locale. As a consequence, traffic patterns and congestion resulting in longer travel time increases the level of exposure. Even with relatively low levels of urban background pollution, a significant traffic slowdown can lead to a similar exposure when compared to standard traffic conditions coupled with high urban background NP and UFP concentrations. Natural and anthropogenic NPs and UFPs were sampled and compared in rural and urban areas by XRD and advanced microscopies to improve outdoor air quality in touristic zones. The results presented in this study illustrate that the method of sampling and analysis of historical structures is a promising technique for the non-invasive and qualitative screening of NPs where there are industrial, vehicle-based, and other anthropogenic emission sources (such as agricultural activities). Nanomineralogy assists in the study of compounds harmful to children, especially regarding reduced cognitive performance, strain on the cardiovascular system, increased risk of early mortality, heat exhaustion, syncope, and cramps.

Significant urban and tourism-based contamination of the air quality surrounding Belgium's Steen Castle and differing levels found near Fort van Schoten have been detailed in this study. The high traffic areas have proven to be a significant source of the pollutants: chromium, antimony, nickel, vanadium, cobalt, chromium, zinc, as well as other PHEs. The steady rise of tourism in the area has led to a resulting rise in localized levels of pollution. Continuous analysis and study of this pollution should be utilized as a baseline for the assessment of limits in the growth of tourism allowed on the island. This can help to protect both the local environment and overall public health. In view of the results obtained, it is recommended that officials clean the black crust from Steen Castle surfaces where it is present. The information presented can help to adopt protection or restoration measures to preserve historic cultural heritage. The dates of this work also show that network-wide aggregated indicators, namely average travel time and average pollution level, only provide a rough estimation of exposure. For precise assessment, it is necessary to use systems that determine the travel times in a given direction on particular roads while at the same time ensuring representative monitoring of air quality on those same roads. This work offers key information that will inform air quality policy as the chemical composition of urban atmospheres change in the future. Most notably, sulfur dioxide emissions are being reduced across many cities. This makes it increasingly likely that urban pollution will be dominated by emissions of nitrogen oxide (a precursor of nitric acid) from road traffic and by ammonia from agriculture for the coming decade or more.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsf.2020.07.003.

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