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A study of dust airborne particles collected by vehicular traffic from the atmosphere of southern megalopolis Mexico City

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Abstract

This study was made to assess airborne dust by sampling particles trapped in car air filters (CAFs) of Mexico City. The CAFs dust was analyzed by optical microscopy and SEM–EDX. The optical microscopy revealed that the dust contains organic matter; insect and plant debris and inorganic matter; quartz sand, plastics and polystyrene. This material was classified in different sizes (from 10 µm to 76 µm). Particulate matter (PM) trapped within the filter fiber arrangements were observed by SEM–EDX. PM of Mexico City was characterized as mainly agglomerated particles and fine particles. Agglomerates were mechanically disintegrated and main components were determined finding elements such as C, O, Si, Al, Ca and Fe. An impaction test was implemented to have insights into how agglomerates probably hit the filter surface, disintegrate and reintegrate other agglomerates. Pollen particles were frequently associated with agglomerated PM; its composition was analyzed, finding Pt on its surface among others. Likewise, the insect debris presented plenty of PM adhered to its surface. This work validates that CAFs are a simple, cheap and adequate sampling approach for further urban air quality evaluations.

Keywords: Air, Pollution, PM, Pollen, Insect, SEM–EDX, Microscopy

Introduction

Air pollution remains a major issue in many cities, local pollution sources such as vehicular traffic and fuel combustion for cooking and heating are main causes (Dockery et al. 1993; Krzyzanowski et al. 2014).

As in many large cities, and especially in ones located in valleys with limited ventilation, Mexico City experiences air pollution problems. The air in Mexico City is impacted by pollution coming from sources like industrial processes, power plants, traffic emissions and wind-blown dust from a dry lake basin. Particularly, in Mexico City the average visibility of some 100 km in 1940s is down to about 1.5 km. The city generally remains enclosed by a dense layer of persistent fog that covers almost all the time, especially during the winter, and there is great concern among residents and visitors about the effects of suspended particles on health and exhaust particles, whether diesel or gasoline engines, are primarily responsible for black smoke or permanent smog (Edgerton et al. 1999).

World Health Organization suggested that more people are killed prematurely by the effects of vehicular emission particles than from car accidents (World Health Organization 1999). Pollutant emissions have been continuously increasing in developing countries and as urban air quality declines, the risk to human health is even greater (World Health Organization 2018).

Particles exist in the atmosphere in many forms, from sub-micron aerosols to clearly visible grains of dust and sand (Shyam et al. 2006). The chemical pollutants and dust emitted into the air depends on the specific sources of emissions. Moreover, the chemical composition of dust in the air is influenced by the coexisting pollutants, and the products of their transformations in the air; due the dust is a surface adsorption for them. The oxides of

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sulfur, nitrogen and ammonia are the sulfate, nitrate and ammonium ions present in air pollution, they can be associated with dust particles on their surface and it has been observed that the dust also shows the presence of heavy particles of metals and hydrocarbons (Kelly and Fussell 2012). Specific threat to air quality and human health is the fine fraction of particulate matter, with an aerodynamic diameter. PM is a portion of air pollution that is made up of extremely small particles and liquid droplets containing acids, organic chemicals, transition metals, and dust particles. Its content in the air is the result of a balance between dust emission and the amount of dust removed from the air (Kelly and Fussell 2012). PM is usually characterized by its diameter ranging from nanometers (nm) to several tens of micrometers (µm) (Harrison and Yin 2000).

Particles with a diameter less than 10 µm are classified as PM_{10}. Particles with diameters less than 2.5 µm are defined as $PM_{2.5}$ or fine particles. Particles with diameters between PM_{10} and $PM_{2.5}$ are known as the coarse fraction. Fine particles scatter light very efficiently and therefore play a major role in visibility impairment (Chan et al. 1999). They are also able to penetrate deep into the human respiratory system and can be absorbed into the blood, interfering with oxygen gas-exchange in the lung alveolar region. The smallest and most numerous particles have diameters < 0.1 µm and are known as ultra-fine particles. Fine and ultra-fine particles are both considered major issue to human health (Ki-Hyun et al. 2015; Terzano et al. 2010).

It has been shown that the size of the airborne particles and their surface area determine the potential to elicit inflammatory injury, oxidative damage, and other human and ecotoxicologic risks difficult to predict (Valavanidis et al. 2008). For example; the exposure to PM in ambient air has been linked to several health outcomes, ranging from modest transient changes in the respiratory tract and impaired pulmonary function, through increased risk of symptoms requiring emergency room or hospital treatment, to increased risk of death from cardiovascular and respiratory diseases or lung cancer (Soukup and Becker 2001; Anderson et al. 2012).

The size of the particles or the aerodynamic diameter not only determines the origin of the particles, their transport to the atmosphere (Srimuruganandam and Nagendra 2012) or how they are deposed in the respiratory system (Löndahl et al. 2006), but also determines the method to perform their sampling. There are now several models available for sampling PM (Wilson et al. 1980), but it is difficult to compare them.

A precedent paper suggests that car filters (CAFs) capture a mixture of atmospheric particles, which can be analyzed in order to monitor urban air. Thus, the continuous availability of large numbers of filters and the retroactivity associated to the car routes suggest that these CAFs are very useful for studying the high traffic emissions zones within a city. CAFs capture a complex mixture of irregular dust particles in the air with physical properties that vary in shape, size and density (Heredia-Rivera and Rodriguez 2016).

The capture of particles by solid objects, both synthetic and organic, occurs by a variety of impaction processes. If a particle of dust moves along with the air flow near the surface of an obstacle and the particle is too large to follow the directional change of the air flow, then it can hit its surface, this process is called impaction. Many studies assume such particles have a spherical shape to simplify the mathematical model to describe their motion. However, the adhesion of these small-scale particles to surfaces of smooth and rough structures suggests there are many factors affecting affect their dynamic behavior (Yang et al. 2018).

The motion of airborne particles in the atmosphere forms a dust cycle which consists of processes of emission, transport and deposition. Dust deposition is the transport of particles from atmosphere onto any earth surface. This process is influenced by factors related to the proprieties of the airborne particles, atmospheric flow conditions and the underlying surface characteristics. The particles are collected by the surface due to impaction, interception and Brownian motion. They are either retained to or rebounded from the surface, depending on a combination of surface and particle properties (Beckett et al. 1998).

Despite a considerable amount of basic research, a full understanding of exhaust particulate matter, its physical and chemical properties, and its effect on human health and the environment is still lacking.

The aim of the present work is the detailed investigation of the morphological and microstructural characteristics of the airborne dust particulate matter collected from CAFs in the Mexico City, determining their size variation, diversity and chemical composition by means of SEM microscopy and EDX analysis. At the same time, perform a detailed analysis of how the direct impact of these particles can affect the regular dynamics that small organisms establish in large metropolis.

Methodology

Study area

The CAFs were collected from service agencies (Ford, Chevrolet, Toyota, and Nissan) located in the south of Mexico City (19°18′ 26.2″ N, 99° 12′ 42.7″ W). The CAFs sampled were selected from vehicles that circulate at the south of the city, Fig. 1a provides information of the lifetime route of five randomly selected vehicles.

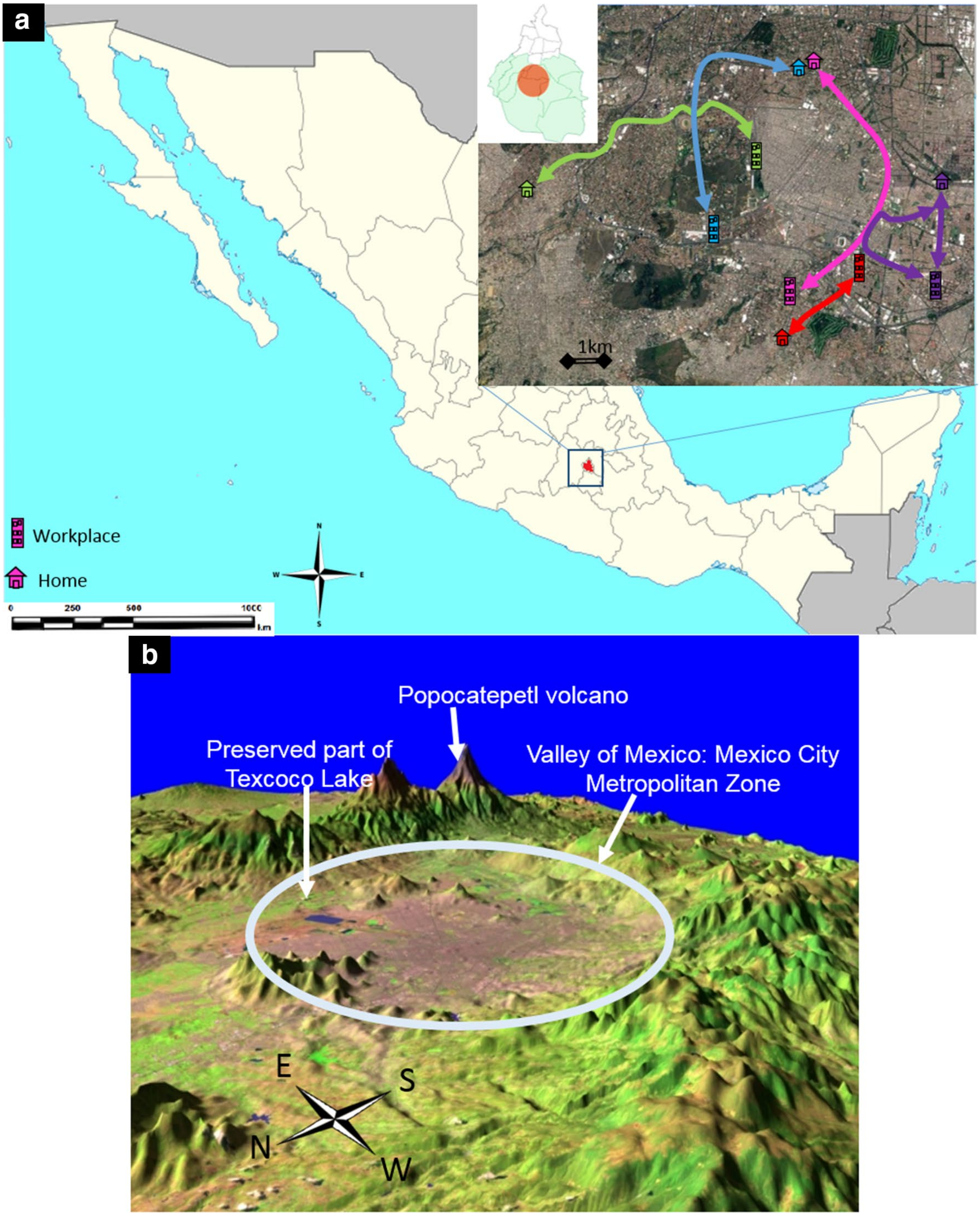

Fig. 1 **a** Mexico City location and study area. Each color represents a different lifetime route of five vehicles. **b** Topography (high vertical exaggeration) of Metropolitan Zone of Mexico City (Credits to: NASA/Goddard Space Flight Center Scientific Visualization Studio)

Mexico City is a megalopolis in Latin America with a population around of 8.9 million (INEGI 2015) and a surface of 1495 km^2. There are about 4.7 million of motorized vehicles circulating all around the metropolitan area (INEGI 2016). Mexico City transit system is composed by heavy traffic asphalt roads. The city is situated in a valley surrounded by mountains reaching elevations of 2240 meters above sea level (Fig. 1b). The Mexico City air quality standards are as follows: PM_{10} (annual mean: 50 μg/m^3; daily average: 120 μg/m^3); $PM_{2.5}$ (annual mean: 15 μg/m^3; daily average: 65 μg/m^3); O_3 (1-h average: 110 ppb; 8-h average: 80 ppb); SO_2 (annual mean: 30 ppb; daily average: 130 ppb); NO_2(1 h average: 210 ppb); CO (8 h average: 11 ppm) (Rivera-González et al. 2015).

The Metropolitan Zone presents a template rainy climate, with an average temperature of 16.6 °C, maximal temperatures can reach 28 °C and the lowest ones can be close 0 °C or even −4 °C in peripheral areas.

Sample collection

Mexico City emissions are one major problem for the air quality. Some policies have been established in order to decrease them; this includes an annual inspection of vehicles emissions and a 1-day circulation restriction based on the plate number, among others. However, these policies seem to be not enough to solve the air pollution problem. Car condition, for example; age and maintenance are an aspect that Mexico City is aiming to control seriously. Strict restrictions have been applied to old vehicles and people prefer to replace them more frequently with new cars. Manufacturers of new cars in Mexico offer engine warranties if the buyer obtains the preventive maintenance service. The service agencies recommend changing CAFs between 6000 and 10,000 km.

The role of CAFs, which are located between the air intake and the engine, is to protect the engine from air particulate matter. For sampling, CAFs from vehicles that sought service at authorized agencies with an average record of 11,924 ± 1694 km, from 2015 to 2016 models were collected. The recollection time was between January and March 2018. 10 CAFs were directly removed from the plastic box connected to the throttle body with an intake duct. The CAFs were then placed in sterilized plastic bags and stored in the laboratory at 4 °C.

Methodology to remove particles from the CAFs

The collected CAFs were reviewed to rule out any perforations. The particles collected by the filters were divided into two categories; the first consisted of those particles that could be removed by friction. The second is that of those adhered particles which were not removed by friction.

The first group was separated by shaking the filter on a vortex plate, any extra material or particles on the filter were detached gently with a fine brush. Individual samples were over-dried at 40 °C and 20% relative humidity for 24 h, and then sieved through a 200-mesh sieve to remove other oversize materials. The dust recovered was weighed using an analytical balance. After sieving, five fractions were collected and sorted by the following particle diameters: 74–60 μm, 59–56 μm, 55–44 μm, 43–20 μm, and 19–10 μm. Until analysis, sub-samples were weighted and stored in polyethylene flasks in a cool and dry place. The separated particles were observed using transmission and reflected light microscopy (model illuminated with optic fiber ring and equipped with a Panasonic GP-KR222 analog camera (Panasonic, Tokyo, Japan) and frame grabber (Encore Electronics, Los Angeles, CA, USA). Image analysis was performed using a micrometer rule (200 line/mm) and the Image J software information about the program can be found on http://rsbweb.nih.gov/ij/. To study the particles deposited on the CAFs, the cellulose filter was removed from the metallic and polyurethane foam supports, and small pieces of filter were studied by scanning electron microscopy.

Agglomerates

Agglomerates fragmentation due to collisions against CAFs when vehicles circulate around the city was evaluated by mechanical launch against a rigid surface to determine how this inertial impaction affects the original structure of the agglomerate.

Scanning Electron Microscopy and EDX from Particles Adhered on the CAFs

For SEM sample preparation, filter pieces of about 0.5 cm^2 were cut with scissors from the center of each sampled CAFs and mounted on 12.5 mm SEM stubs for gold coating. A very thin film of gold (Au) was deposited on the surface of each sample using a Gold Sputter Coater (Desk II) vacuum coating unit (Denton Vacuum LLC, Moorestown, NJ, USA). The SEM–EDX analysis of morphology and chemical composition of individual particles was carried out using a computer-controlled field emission SEM instrument (JSM-6330F, JEOL, Peabody, MA, USA). The EDX was carried out for each elemental analysis using the line scan analysis technique, and the present elements were both qualitative and quantitatively measured (Oxford INCA X-Act, Oxford Instruments, Buckinghamshire, UK). Particle counting was performed using the Image J software. Only particles larger than 0.2 μm were counted. For quantitative element analyses, EDX spectrograms were recorded and the weight percentage of each element present in the spectrum was identified. As mentioned above, the CAFs samples were gold coated. Therefore, the gold data of EDX cannot be used to estimate the quantitative elemental analysis, the Au contribution was manually subtracted during the evaluation of the EDX spectra. Three new CAFs that were purchased from official service agencies were used as controls and were prepared and analyzed identically to the experimental samples.

Biological particle analysis

Palynological analysis of the organic material trapped on the CAFs was implemented according to the method used for melissopalynology. Briefly, 0.1 g of dust was placed into 10 mL test tubes and washed by centrifugation and decantation using distilled water. Then, a 10% potassium hydroxide solution was added to the residue, which was then warmed at 70 °C for 10 min with occasional stirring. The material was filtered on a 300 µm filter, centrifuged twice for 5 min at 3000 rpm, and then decanted twice. The residue was treated with 7 ml acetolysis mixture (9:1, v: v, acetic anhydride and concentrated sulfuric acid). The sample was warmed to 80 °C for 5–10 min with occasional stirring. Next the acetolysis mixture was removed by centrifugation and decantation. The residue was washed with ethyl alcohol and transferred to an Eppendorf tube. Two drops of glycerin were added, and the open tube was placed into an incubator at 40 °C for 12 h. The slides were then prepared using the method of Jones (2014). They were observed with light microscopy. Some positive samples were prepared in a similar way for scanning electron microscopy as described in the paragraph above.

Statistical analysis

The particle measurements were compiled for statistical analysis; values are expressed as means ± standard deviations. An analysis of variance was used to determine the statically significant differences between the means of the particle size; a Tukey honestly significant difference (HSD) test performed on significant ANOVA findings to identify statistically significant pairwise differences between size diameter ranges.

The agglomerate fragmentation was analyzed by principal component analysis, the active variables were the elements detected by SEM–EDX and the observed variables the fragmentation fractions.

Results

Optical microscopy analysis of the particulate material

The optic microscopy analysis of particles found in CAFs, two major groups were separated based on their nature: inorganic or organic origin particles. Inorganic materials were mainly dust particles, clay, quartz sand, plastic fibers and polystyrene pellets, (Fig. 2). As for the organic matter; we found insect heads, legs, wings or the whole organism and vegetal tissues such as leaves and seeds, (Fig. 3).

The analyses of the CAFs revealed that the average weight of the retained dust was 0.62 ± 0.48 g (n = 10).

Upon closer inspection of the separated particles from the organic material, such as fragments of insects and leaves, exhibited a considerable amount of particulate material adhered to its surface, (Fig. 3a–f). These particles were mostly of a large size with equivalent diameters ranging from 74 to 10 µm.

The particle material size distribution analysis was performed by defining their size ranges and frequency with a following particle diameter: 74–60 µm, 59–56 µm, 55–44 µm, 43–20 µm, and 19–10 µm. The particle size that was found 74–60 µm and 55–44 µm were in the same frequency. The 59–56 µm and 43–20 µm also presented practically an equal frequency between them, but slightly lower. There were not significant differences between these diameter ranges, in contrast, the range of particle sizes 19–10 µm showed a significant lower frequency as displayed in Fig. 4.

A close view of the particle material found in CAFs

In depth analysis by SEM–EDX of sections cut out from a CAFs showed that they are composed by fibers arranged randomly with diameter 17.5 ± 7 µm, n = 50, and cavities much larger than fiber diameters (36.24 ± 9 µm, n = 50, Fig. 5a, b). Diverse PM forms were found trapped by these fibers, the particles retained had different sizes; with equivalent diameter range from 18 to 0.7 µm. The agglomerates were the main visible component of these particles (Fig. 5b–d). They always were adhered to the fibers with an equivalent diameter less than 20 µm. There is also evidence of pollen grains trapped within other agglomerates (Fig. 5c), very fine particles (< 5 µm), packed soot agglomerates (Fig. 5e) and black carbon accumulations on fiber surface (Fig. 5f).

PM agglomerates and fractions

The PM agglomerates that were removed from the CAFs were bigger than those that stayed adhered to its fibers (60 ± 24 µm, vs 16 ± 4 µm, n = 50). A single agglomerate, representative of those adhered to the fibers of the CAFs is observed in (Fig. 6a). It is formed by particles that have different morphology and size, attached to each other in a seemingly random arrangement.

The composition analysis of agglomerates revealed that in addition to carbon and oxygen, the particles contain high amounts of Si, Fe, Al and Ti (Fig. 6b).

Figure 7c shows initial agglomerate that was launched against to a cellulose paper surface, it shattered into smaller fractions of different sizes. This fractions dispersed into different directions after the impact, each piece of the initial agglomerate presented a different appearance than the original particle. The arrows on Fig. 7 show the direction in which each fraction was dispersed after the impact.

Figure 7a represents an amplified image of the biggest broken fraction, signaled on Fig. 7c, this piece presented a relatively intact, smooth and homogeneous appearance.

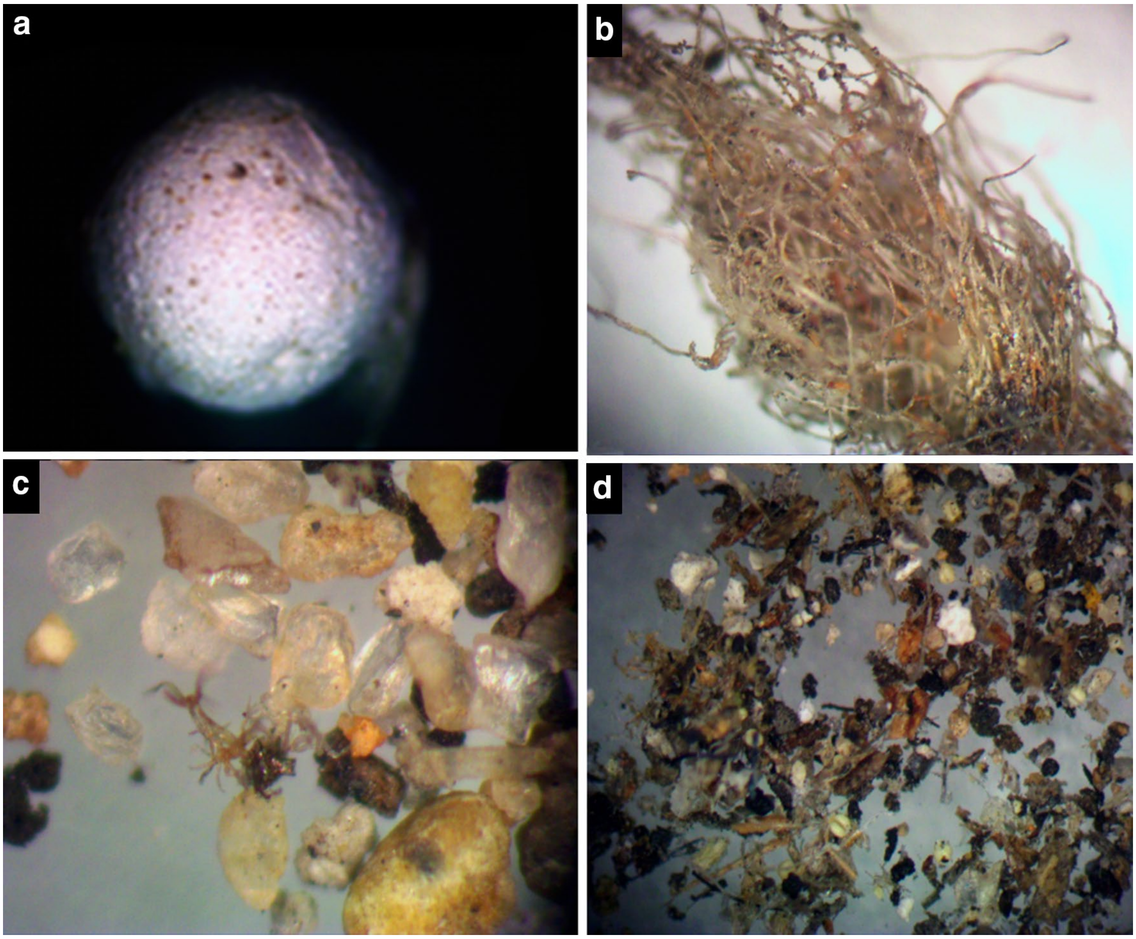

Fig. 2 Inorganic material sampled from the CAFs. **a** Polystyrene pellet with incrusted minor particles. **b** Fibers. **c** Quartz sand. **d** Various particles

In comparison to this fraction, the other agglomerate fractions were more fragmented and dispersed, Fig. 7b, d. The agglomerated fractions looked mostly grainy, roughed and had an assorted appearance.

The SEM–EDX analysis carried out to determine the composition of the scattered fractions, (Fig. 7a–d), established a distinctive pattern of C, O, Na, Mg, Al, Si, K, Ca, Ti, Fe, and W.

The principal component analysis from fragments showed two factors with 100% of the overall variance. F1 shows the maximum variance of 64.95% and F2 represents 35% of the variance (Fig. 7e).

Fragment B presented high concentrations of C, Ca and Fe while fragment A, was characterized with the main presence of O, Mg, Ti and W.

Fragment D contributed to both components; however, it showed a significant amount of Si in its composition.

Biological materials trapped by CAFs

Pollen grains were another example of airborne particles found either in CAFs (Fig. 8c) or trapped by some organic tissues (Fig. 9h, i). Pollen grains were normally associated with PM agglomerates and had smaller particles adhered on their surface. Pollen morphologies were observed (Fig. 8a–e) and analyzed in terms of composition.

The main composition profile of pollen grains found in CAFs was nearly 60% weight carbon and $\approx$30 weight % oxygen. Surface analysis indicated the presence of Si, Ca, and Pt as minor elements. Less common elements were identified in pollen grains surface such as Fe, Na, Al, Mg and K.

After fragmentation of a pollen grain, the internal composition conserved similar proportions of carbon and oxygen, nevertheless Pt that was only found in the surface (Fig. 8g).

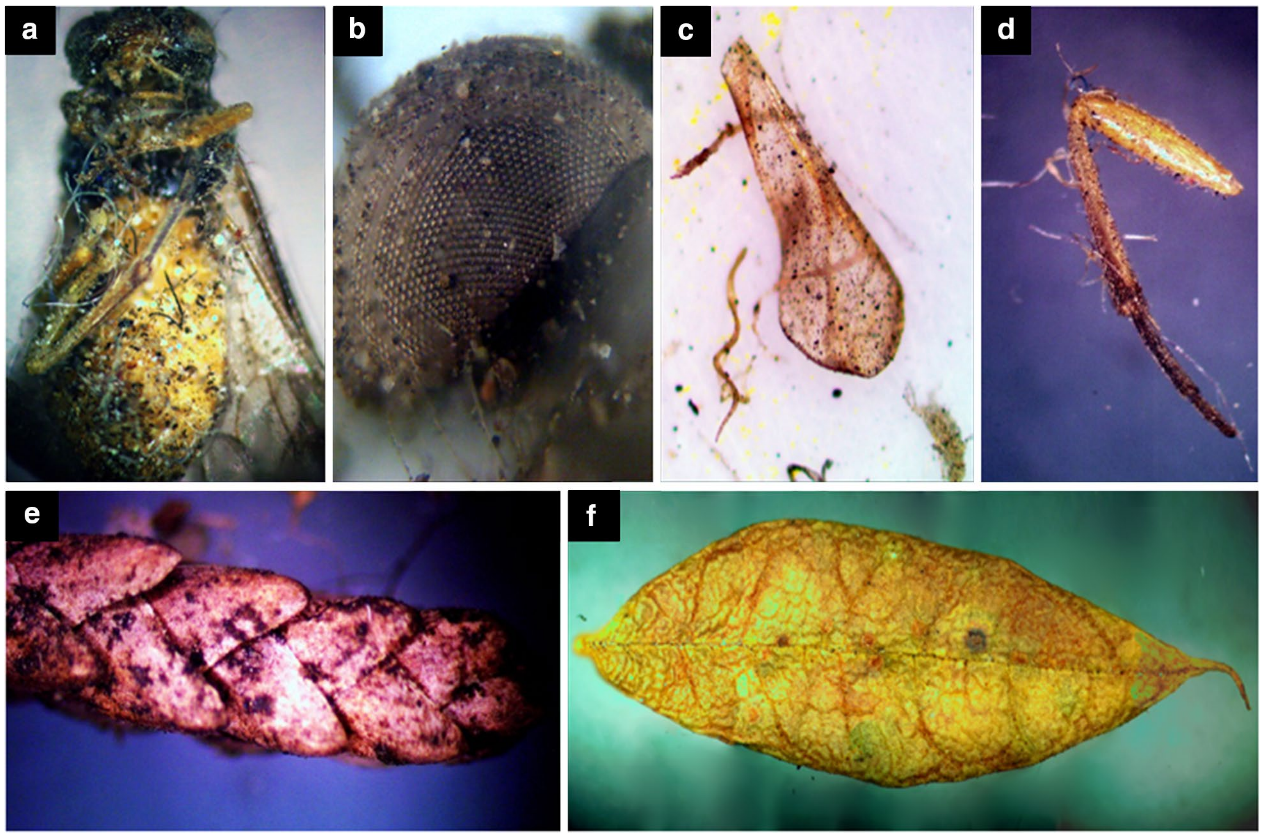

Fig. 3 Biological materials found in CAFs. **a** Fly covered by particles. **b** Fly compound eye. **c** Insect wing. **d** Insect leg. **e** Plant spike. **f** Leaf

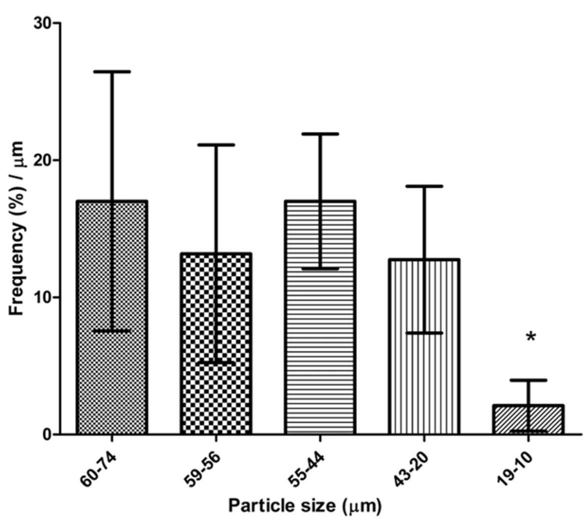

Fig. 4 Frequency and size distribution of particles taken from CAFs. Each bar represents the mean ± SD, asterisk means significant difference (Tukey's HSD, $p < 0.002$), $n = 10$

Particles found in flying insects

After a deep inspection of the organic material trapped in CAFs, diverse insect parts and full exoskeletons were retrieved, it was noted that a great number of particles were bound or adhered to its surface. The SEM analysis was carried out it was found that these organic materials contained PM.

From the insect parts retrieved and analyzed it was found that they were mostly upholstered with particulate material. Figure 9e shows external tissue of a fly and how the PM was accumulated on the exoskeleton covering almost every available surface.

Several particles were retained in the wings, most of this PM accumulations where located around campaniform sensilla (Fig. 9a) and especially at wing edges (Fig. 9b). Fly abdomen was another site where PM was clearly adhered and easily observed between the abdomen segments and the posterior part. Claws (Fig. 9d) and the superior part of the head (Fig. 9f) showed the

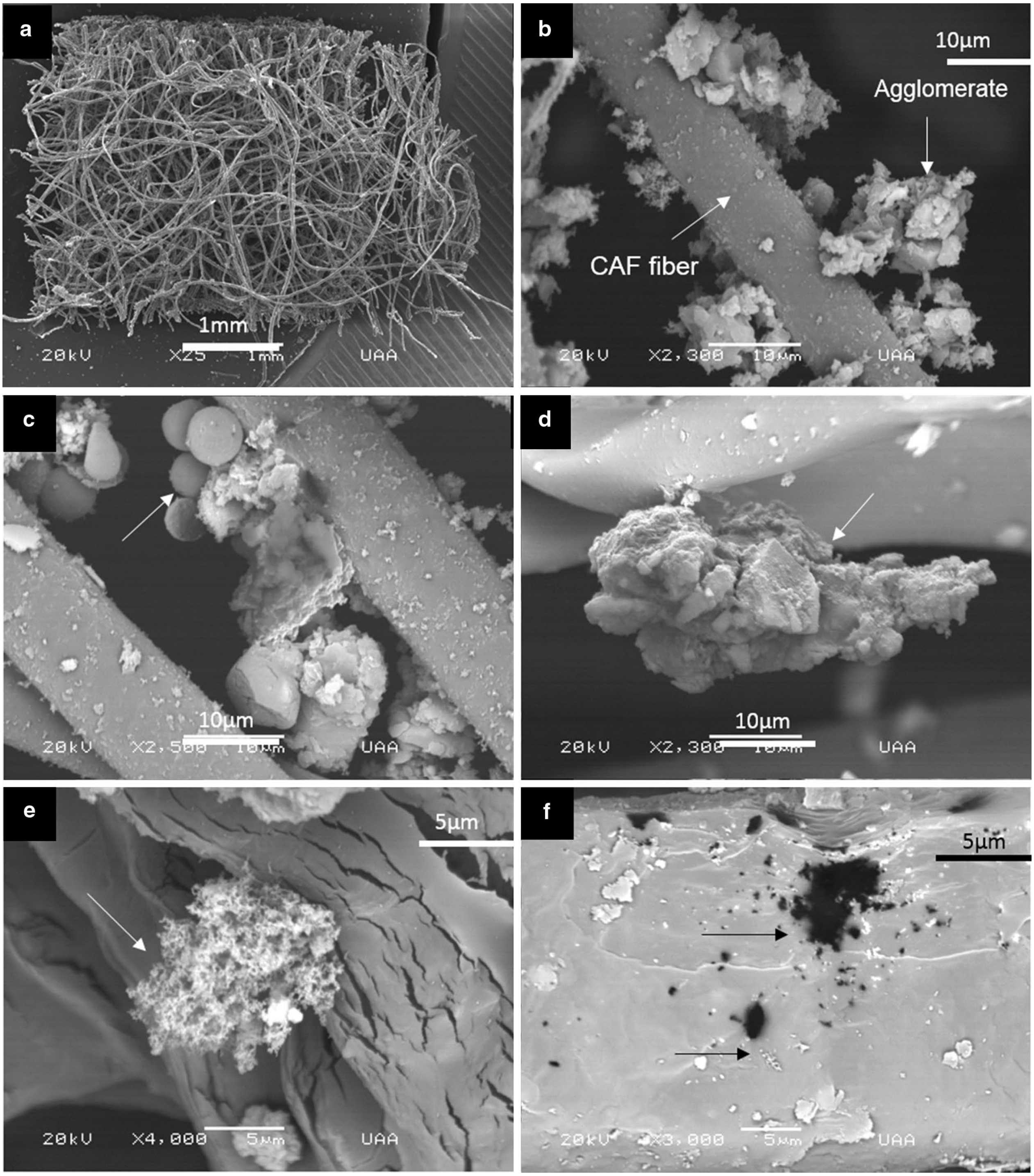

Fig. 5 SEM analysis of CAFs samples. **a** CAF small section. **b** Individual fiber. **c** Different types of PM retained by CAFs fibers; pollen grain, fine particles, PM agglomerates. **d** PM agglomerate attached to a single CAF fiber. **e** PM agglomerate exhaust from combustion. **f** Dark spot on fiber surface

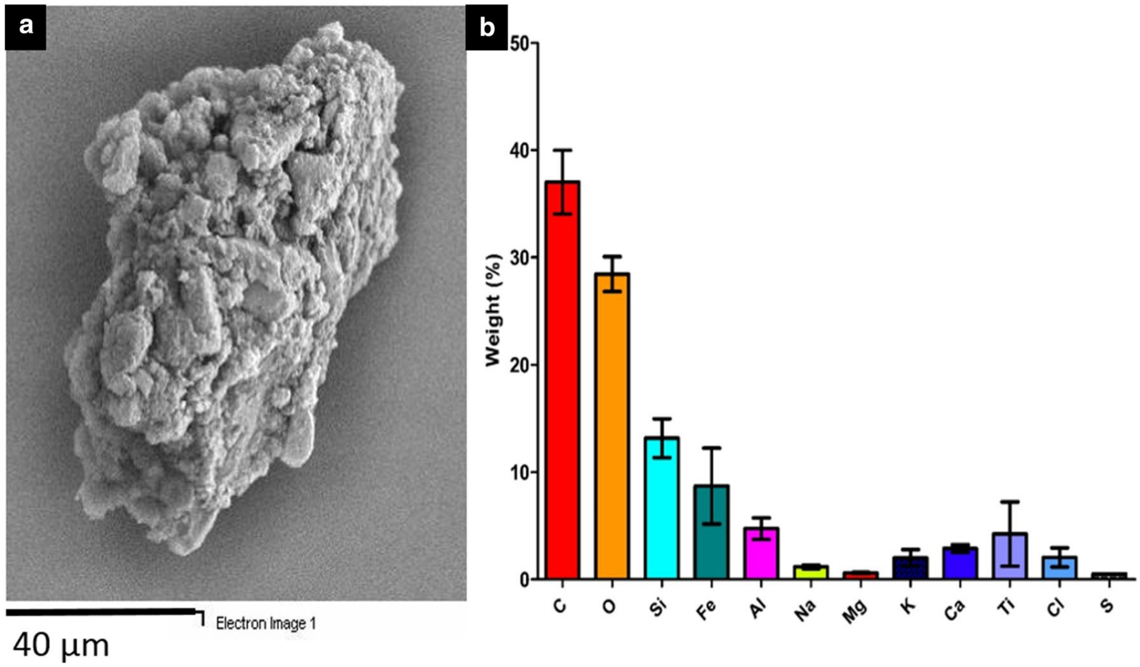

Fig. 6 **a** SEM analysis of a PM agglomerate isolated and deposed on a cellulose sheet. **b** Mean chemical composition of the agglomerates in weight % (± SD), n = 20

highest concentrations of PM, these particles where mostly deposited on pulvilli, all over the compound eye or close to campaniform sensilla. PM was also appreciated around the mouth zone as shown in Fig. 9a.

Figure 9g indicate that PM was widely present as agglomerates incrusted all over insect body. Among other PM components, pollen grains were identified as shown in Fig. 9h, and they were also present associated with PM agglomerates (Fig. 9i).

A deeper view of compound eye showed the presence of different sizes of, agglomerates and individual PM are well distributed on the surface eye (Fig. 10a–c). The Fig. 10b linear composition profile show high amounts of carbon and oxygen, and traces of different elements like Na, Cl, Ca, Al, Fe, Si and Pt, being the last two found in important proportions, Fig. 10d.

Image J was also used for analyzing a picture (Fig. 10c) of the fly compound eye, the gray intensity varying along a line drawn on the image (Fig. 10f) represented an approximative one-dimension analysis of the compound eye surface and its adhered PM. The height and the amplitude of each pin define the size of the attached particles.

The compound eyes showed a clear and typical hexagonal arrangement of ommatidia, a close inspection of interommatidial areas showed a high accumulation of PM, which could be classified as fine particles (in this case with < 1 µm diameter), (Fig. 10e).

Discussion

Context

Environmental pollution, but especially air pollution is one of the most worrying issues today. Urban areas are the main sources of air pollution (Edgerton et al. 1999; Mage et al. 1996). The pollutants once released into the atmosphere are scattered by air currents with no distribution limit, reaching and depositing in unexpected places (Vega et al. 2010; Fromme et al. 2007). The particulate material suspended in atmosphere contributes importantly to air pollution and affects the health of all those organisms living either in urban areas (West et al. 2016 and references in it, Sanderfoot and Holloway 2017) or in natural ecosystems (Mohapatra and Biswal 2014; US EPA 2018).

For the study of air PM, different sampling methodologies have been used. The devices to collect the PM consist of sophisticated and expensive designs, based on principles such as inertia, filtration and centrifugation. These devices are usually not only limited by their specialized mechanisms but also when it comes to perform several samplings in wide areas. Geiß et al. (2017) indicated that the inclusion of PM10 in the mixing layer of Berlin's atmospheric aerosol varies significantly from site to site, is important to remark that CAFs have proven to be effective in obtaining reliable information. They sample PM and coarse particles from different zones of the city since they are in continuous movement by urban

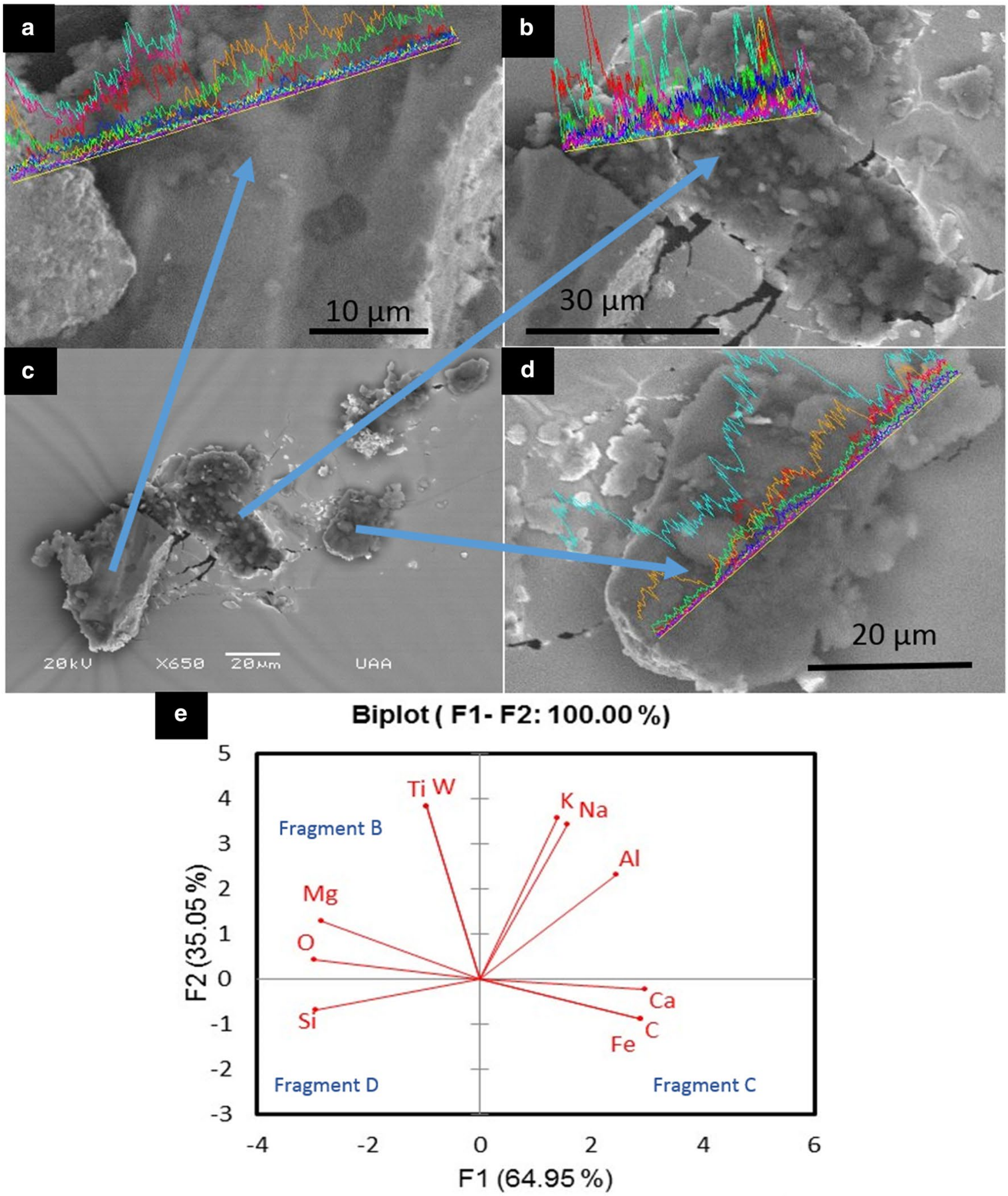

Fig. 7 Fragmentation of PM agglomerates. **a** PM agglomerate. **b** Amplified image of the biggest broken fraction. **c**, **d** Fragmented fractions. **e** Principal component analysis

roads and exposed to spots constantly contaminated by vehicular traffic.

Particles retained by CAFs

It was confirmed that the sampling CAFs had the random fiber arrangement typical of the High Efficiency Particulate Air (HEPA) filters (Fig. 5a). The particles retained by the filters are varied in size and origin. In our case, vegetal, animal and inorganic particles were found. The visual analysis with an optical microscope allowed us to distinguish inorganic particles such as grains of quartz sand, clays, soot, plastic fibers and polystyrene pellets. Components such as quartz and clays can come from natural activity since in Mexico City there is a wind circulation strongly

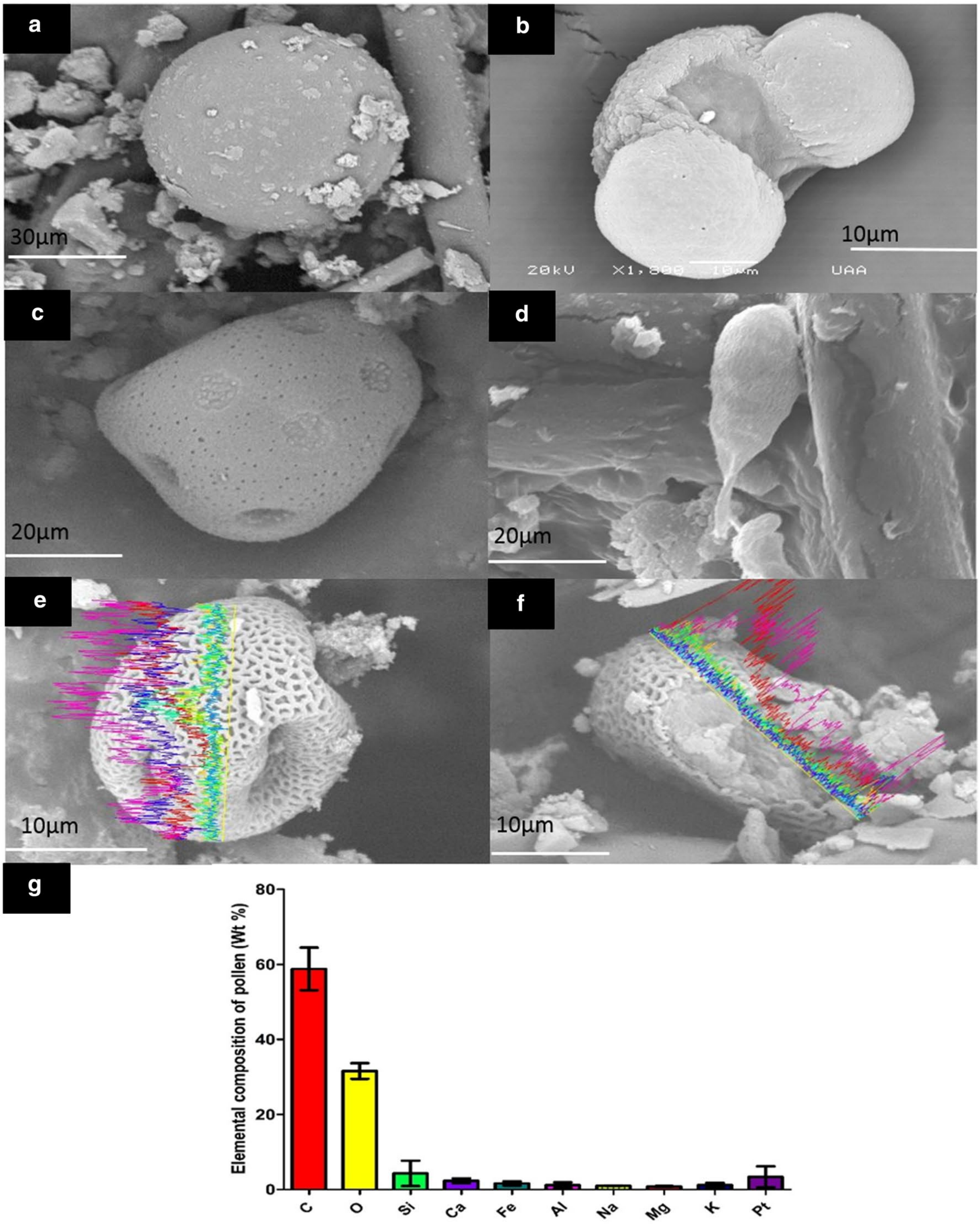

Fig. 8 SEM analysis of pollen grains. **a**–**e** Different pollen grain morphologies. **e**, **f** Pollen linear composition profile analysis. **g** Mean surface composition in weight % (± SD), n = 20

influenced by its location (De Foy et al. 2005). Mexico City was built on the sediments of an artificially dried lake, is surrounded by mountains and is relatively close to active volcanoes. The air flow keeps moving not only the dust or organic materials generated by nature, but also the vehicular emissions that are the main source of particulate material in urban areas (Ho et al. 2003; Quijano and Orozco 2005).

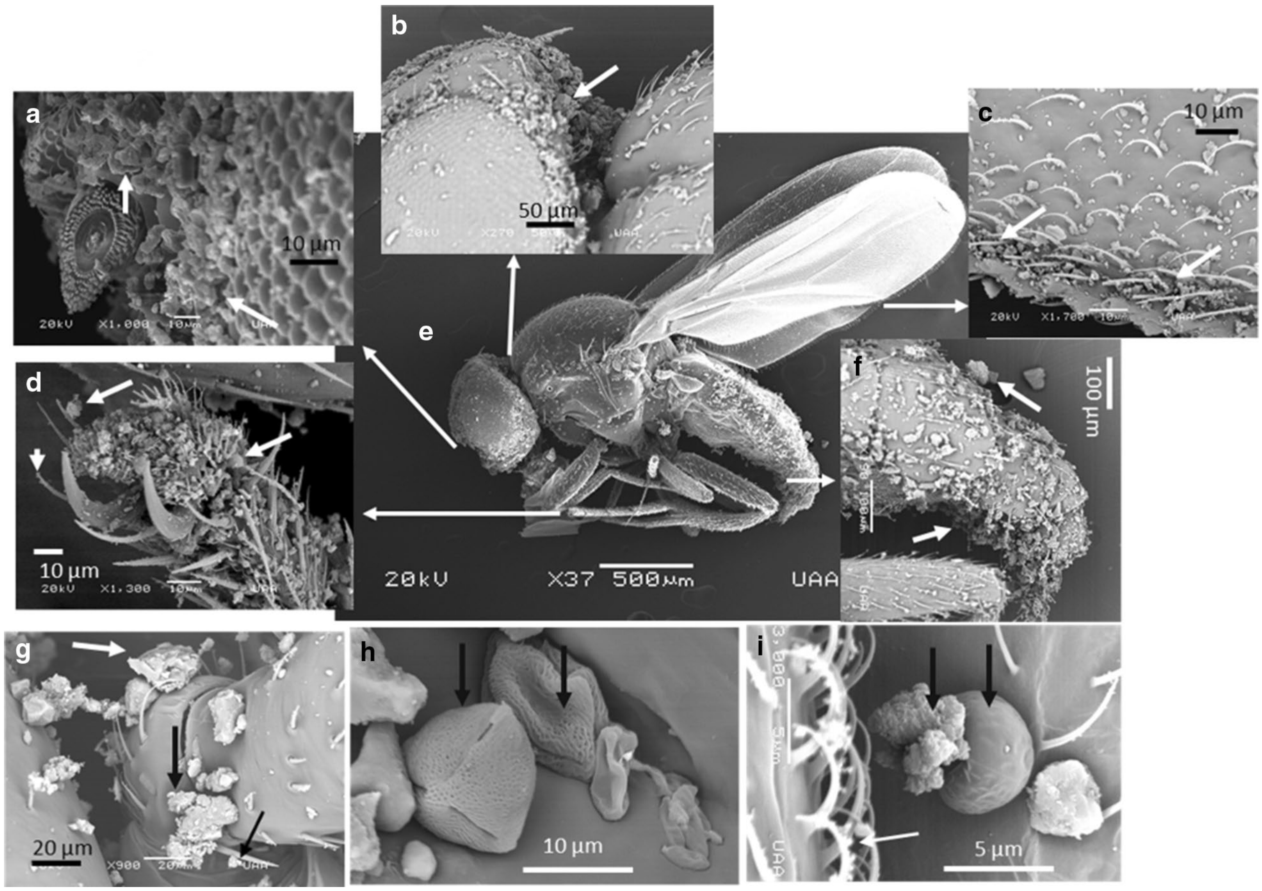

Fig. 9 **a** SEM images montage from a fly found in CAFs. **b** Close view of mouthparts, **c** thorax-head junction, **d** left wing, **e** leg with bristles and claws, and **f** abdomen. **g**–**i** PM agglomerates and pollen retained by fly tissues

In the case of the biological material collected by the CAFs, fragments of leaves, seeds, stems and insects were observed. This type of particles is originated mainly by different biological processes that occur cyclically in nature and that are called primary biological aerosols (Despres et al. 2012). The large metropolises such as Mexico City are not exempt from the release of plant and animal particles as both gardens and homes represent sites where not only anthropogenic activity develops but also coexistence with trees, flowers, flies, ants, bees, cockroaches, etc. Our study confirms a considerable presence of biological material; however, a detailed examination of this material is rarely done.

Studies based on the sampling of CAFs to measure air quality have focused on the monitoring of polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and some heavy metals in $PM_{10-2.5}$. However, the analysis of the coarse and large PM found in the CAFs has only been reported by Heredia-Rivera and Rodriguez (2016). In this previous work, the presence of PM of biological and inorganic origin in the air of the Mexican city of Aguascalientes was also reported.

Removed particles from the CAFs were weighted and distributed by frequency as we report in Fig. 4. By comparing both cases, in Mexico City; the particles of the 19–10 microns range were those found with the lowest frequency particles (< 5%/µm) in the four remaining size groups were found with a similar frequency (~ 10–30%/µm), while in the urban area of Aguascalientes, the most frequent particles were classified in the range of 59–56 microns. It is important to mention that there was a portion that remained attached to CAFs and that was analyzed directly by SEM–EDX. The distribution of semi-uniform particles in the categories greater than 20 µm contained in the dust collected by the CAFs of Mexico City could be due to the fact that the majority were agglomerates, whereas in the city of Aguascalientes the frequency of the highest distribution was concentrated in the category of 56–59 and although the agglomerated were present; were mainly individual particles. This is difficult to explain, however, it can be associated to the fact that Mexico City has a high index

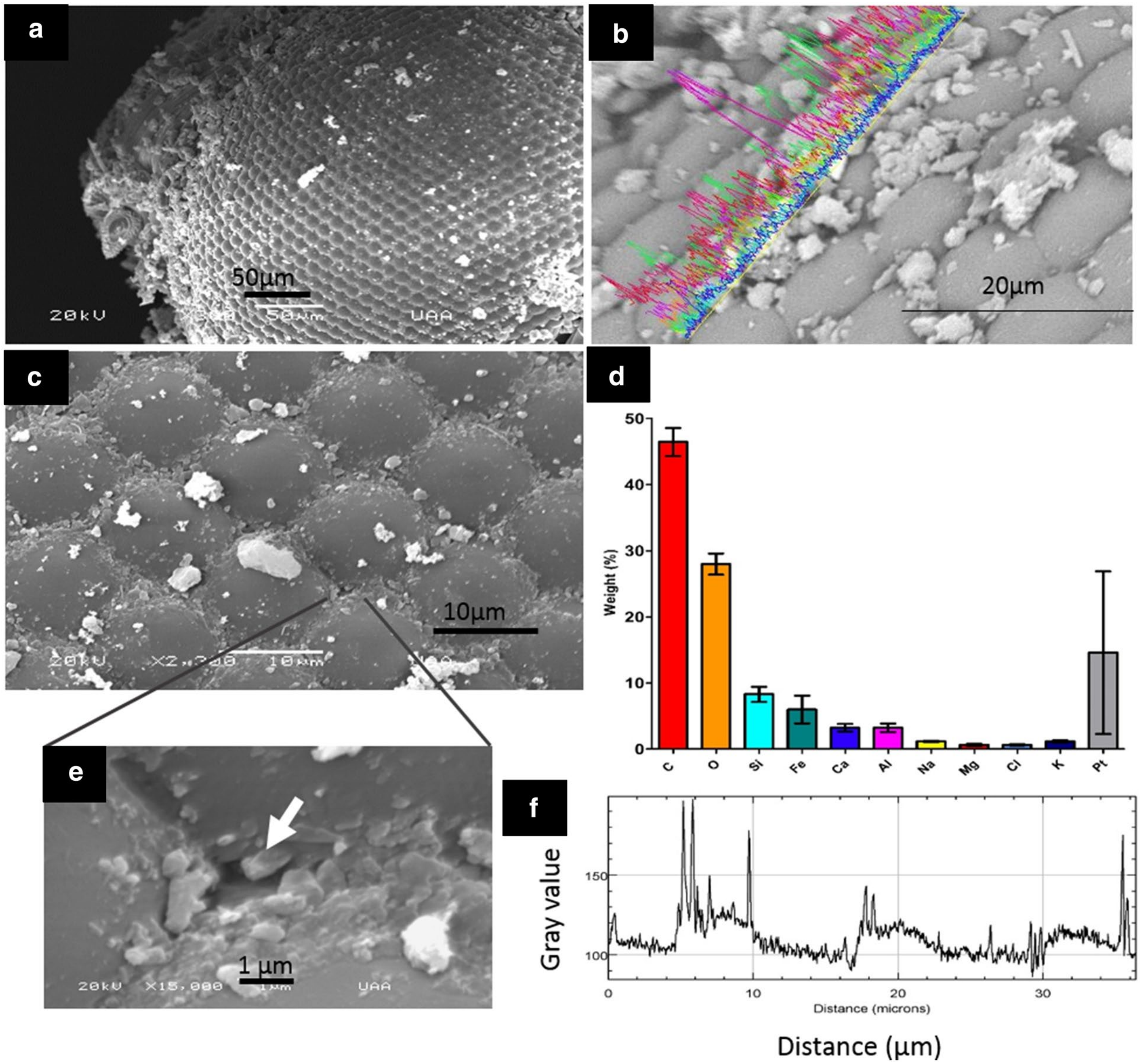

Fig. 10 SEM analysis of a (**a**) fly compound eye. **b** Eye surface zoom on and (**d**) surface chemical composition in weight %. **c** Ommatidia geometric arrangement and **e** fine particles found between each ommatidium. **f** Gray intensity line scan of ommatidia

of vehicular emissions due to heavy traffic and in combination with the climate conditions of the CDMX that favor the formation of agglomerated particles to a greater extent. In this sense, weather conditions are characterized by low atmospheric pressure, it has climates ranging from temperate to humid cold and alpine tundra, the pattern of rainfall indicates that they are more abundant at higher altitude, similar research results were achieved by Majewski et al. (2011). In contrast city of Aguascalientes is a city with less vehicular traffic and a semisemidesertic climate, with sparse rainfall, and average latitude of 1888 meters above sea level.

Mineral and combustion particles analysis

The direct SEM analysis of the filters allowed us to obtain detailed information on the shape and size of the particles retained. The fibers presented agglomerates of heterogeneous composition some within the PM_{10} classification (Fig. 5c, e). On the other hand, fine particles adhered (Fig. 5b–f) and uniformly distributed along the fibers that could fall under the $PM_{2.5}$ classification could be distinguished. Figure 6 shows the order of size of some of the most frequent agglomerates. The particles that make up the agglomerates can vary from relatively coarse grains (Fig. 7a, c) to fragments smaller than 5 microns

(Fig. 7b, d). The C and O were omnipresent in all the agglomerates and could belong to organic compounds originated from the combustion, even soot agglomerates could be observed as those present in the work of Chakrabarty et al. (2014). The soot agglomerates present in the filters have an almost exclusive composition of C and O, which corresponds to the typical profile of the combustion products. Other found elements as Si can be explained by the presence of quartz sand, while Na, Mg, K and Ca are considered as water-soluble inorganic ions which are probably more related to urban PM. The K is used particularly as an indicator of biomass combustion (Andreae 1983) which in Mexico City can be due to forest fires in the surrounding areas, these fires are common and create a significant impact on the quality of the air (Crounse et al. 2009). The Cl can come from organochlorine compounds (Garzón et al. 2015) or from the bed of the Texcoco Lake. The city was founded on an islet in the lake which has been artificially drained since then whereas the urban area has grown. The water in the basin is mostly salty and the lake's bed was exploited for artisanal salt production by pre-hispanic societies (mainly NaCl and Na_2CO_3 with traces of Mg and K) (Williams, 2010; Flores-Hernández and Martínez-Jerónimo 2016) and industrially from 1948 to 1993 (Alcocer and Williams 1996). Part of the lake remains mostly as a salt marsh in the eastern part of Mexico City. In addition, the drainage of the lake has left much of the lake bed exposed to atmosphere causing erosion and frequent dust storms (Alcocer and Williams 1996) so that salts composed of Cl, Na and Mg are not foreign particles in the city's air. The composition of these agglomerates is similar to those found in coastal sites (Moreno et al. 2004).

The Fe, Al, W, Ti and Pt can come mainly from the anthropogenic activity; these elements are part of the automobiles. Platinum, for example, is a usual component in vehicles catalytic converters which are mandatory equipment thanks to the last 3 decades tightening of the rules for the use and sale of cars in the metropolitan area of Mexico City.

However, the asphalt particles are constantly re-suspended in the air due to the displacement of people and vehicles (Shen et al. 2008). Besides, the wind currents maintain a constant PM circulation around the city, so the formation of agglomerates and their disintegration can occur with great frequency in a large metropolis. The composition and the size of the PM that forms the agglomerates are parameters that can be widely influenced by the constant generation and dispersion of particles of different nature that interact randomly in a dynamic environment like the air of Mexico City.

The experiment reported in Fig. 7 allows us to propose a simulation of how agglomerates are impacted on the surfaces of CAFs, asphalt, buildings, people, etc. and their disintegration. The separated elements could easily be resuspended and somehow reintegrated to form other agglomerates again. The analysis of the fracture behavior of the agglomerates is often done to estimate the strength of the bond and identify the weakest link within the agglomerate. This experimental research was limited to the analysis of composition after the impact of the fragments produced due to the fracture. Consequently, it is extremely difficult to capture experimentally each and every one of the breaking events during the fracture process, since it takes place within a very short period of time.

Biological origin particles analysis: pollen

It is important to point out that the area that covers Mexico City is 45% urbanized (north and center), while the rest (south and east) is made up of ecological reserves, forests and cultivation areas (Estrada et al. 2009). In addition, the city includes parks and gardens that are part of 20.4% of urban land. Ecosystems exist in these areas where vegetation and animals interact and develop their life cycle, so it is not uncommon to find biological material in the air. Different types of pollen grains were found in CAFs, which can be originated by trees of the genus *Cupressaseae, Alnus, Liquidambar, Callistemon, Pinus*, and *Casuarina*, or by herbaceous as *Compositae, Cheno-Am, Ambrosia* and *Gramineae* (Terán et al. 2009). The different morphologies of the observed grains are intended for their transport through pollinators or air currents, their adhesion to plant reproductive structures and pollination (ECPA 2013). We observed pollen grains adhered to agglomerated PM (Figs. 5c, 7c) and confirmed the presence of trace elements foreign to the composition of pollen such as Al, Si and Pt. Therefore, it can be considered that its morphology also favors the association of these with air pollutant particles.

Both the particles that make up the agglomerates and pollen are constantly reported as particles that affect health (Valavanidis et al. 2008; Calderon-Ezquerro et al. 2018). Pollen in cities besides being a typical allergen (Kiotseridis et al. 2013) found in the air could also impact health in other ways as it adheres and retains both fine particles and agglomerates.

Biological origin particles analysis: insects

In addition to plant material such as pollen, insects or parts of them could be identified within the material retained by the CAFs, this type of material was similarly identified with that collected and reported in a previous study with CAFs (Heredia-Rivera and Rodriguez 2016). Flying insects were the most found specimens, although terrestrial species were also identified such as ants. It was possible to distinguish relatively intact flies, the SEM analysis of one of these dipterans allowed to visualize in detail its anatomy. The different tissues retained significant amounts of PM including agglomerates material, this material was distributed in all parts of the fly, especially areas such as the thorax-head junction, legs, abdominal folds and compound eyes. These surfaces presented structural characteristics that seem to favor the retention of particles. In general, the epicuticle allowed the direct adhesion of PM and agglomerates, the sensilla retained a good part of the fine particles along its structure, as can be seen in Fig. 9c, d, g and i, likewise they contributed to attach agglomerates as it could be seen in legs and abdomen. The adhesion of particles to sensilla is an interesting fact, since their function is primarily sensory and not to adhere to surfaces as is the case of the pulvilli. It is important to point out that pollen was also present in the tissues of the fly, this pollen could be observed again as an individual unit (Fig. 9h) or associated with agglomerates (Fig. 9i).

In the case of compound eyes where sensilla were absent, the superficial relief allowed the fixation of particles. If we compare the thorax-head or abdomen junction (Fig. 9b) with the compound eye (Fig. 10a), it is seen that the eye is a relatively clean area with respect to the other mentioned regions. However, when a greater magnification of the eye is made (Fig. 10c, b and e) it can be observed that in fact it presents an important accumulation of particles on its surface. The concave shape of the ommatidia allows the formation of deep spaces between them (Fig. 10e), where the predominant presence of fine particles was observed. On the other hand, agglomerates could be observed anywhere on the surface of the eye. The composition of the particles present in ommatidia is similar to the material previously analyzed in individual agglomerates and pollen (Figs. 6b; 7e; 8g, h) since the presence of Al, Si, Fe and Pt was detected. The compound eyes presented a considerable number of particles, although they have been reported to have anti-stick properties (Peisker and Gorb 2010). This anti-adhesion property has been attributed to a decreased real contact surface between contaminating particles and the compound eye. Apparently, fine particles mainly classified within the category $PM_{2.5}$ are not prevented from adhering among the ommatidia due to their small size.

The contamination of insects by PM is a phenomenon that can occur in any city like Mexico City, it was shown that all types of particles accumulate in all parts of the insect body, flying insects such as flies and moths travel long distances and they are frequently exposed to suspended material in the air, in the same way their extremities are in contact with various surfaces where contaminating particles can be present as human waste, flowers, floors, windows, etc. Once the insects are trapped by the CAFs, it is possible that the deposition of particles on their tissues will continue there while the engine keeps working. Future investigations are required to determine this assumption.

Studies have been conducted on the effects of PM containing neocotinoid insecticides on economically important insects such as honey bees, these insecticides are widely used in seed coating and it has been shown that bees are exposed to these substances during seed sowing with lethal effects compatible with the colony losses observed by beekeepers (Tapparo et al. 2012). In the city, PM is abundant and from diverse origin, its impact on urban insect health is possible but remain a study to carry out, so far there are some reports about air PM effects on dogs (Calderón-Garcidueñas et al. 2017) and avian species health (Sanderfoot and Holloway 2017). Insects and their health can serve as biological indicators for indirectly monitor air quality, since as reported by Negri et al. 2015 and by the present work, insects accumulate in one way or another both PM and large agglomerates. It is necessary to implement an appropriate methodology for sampling and quantification of air pollution particles present in insects.

Conclusions

The present work is the first characterization of PM and larger particles by SEM from a sampling carried out by CAFs in megalopolis Mexico City.

The CAFs retained PM and coarse particles of different origin which could be determined and analyzed. We mainly found particles of biological origin and agglomerates of heterogeneous composition. The origin of these particles was linked to the different topographic, climatologic, demographic, economic and ecological characteristics of the city.

The particles found in Mexico City were mostly agglomerates; these agglomerates could vary in size between 1 and 74 microns.

Analyzing PM agglomerates is a complex task since the structure of these particles seems to reconfigure randomly and actively by disintegration and reintegration. One of the most interesting aspects of this study was to verify that the impaction test turned out to be an efficient and one of the very few approaches to analyze in more detail PM agglomerates composition and their probable dynamic when hitting CAFs surface.

It was determined an abundant presence of Si and traces of less common metals such as Pt and W. It was verified that these agglomerates were made up of smaller particles by a fragmentation experiment and analysis of the dissociated fractions. This fragmentation and formation of agglomerates, possibly occurs frequently in the fluctuating air of megalopolis like Mexico City, nevertheless, future studies are required to support this hypothesis.

We demonstrated a characteristic morphology of soot for some agglomerates and they had mainly organic composition. In turn, it was verified that the agglomerates can adhere to pollen or other biological tissues such as insects.

Among the particles of plant origin, in addition to leaves and stem fragments, varied forms of pollen grains were found.

The insects found in CAFs accumulate both agglomerates and fine particles in their tissues; the study through SEM–EDX showed that the fine particles adhere to the omatides and practically covering the entire surface of the ocular apparatus of flying insects. A more complete study is necessary to determine the particle-insect dynamics and the effects of air pollution on their health to reinforce their role as indicators of the air quality in cities and other environments.

Our characterization and composition analysis validates the possibility of estimating air quality by CAFs sampling.

We demonstrated that using CAFs from vehicles with a known route within a metropolitan zone provide general information about air of a city. Each CAF cover a wide area and will definitively sample pollutants that humans are exposed to. Measurements are related to a particular period of the year since CAFs have determinate lifetime. Although the analysis is not performed in real time, several adaptations could be used to evaluate air in shorter periods.

Our results indicate that a pilot evaluation of urban air quality by CAFs is feasible and relevant. A CAF based assessment is potentially more representative, simpler and cheaper than isolated in situ sampling methodologies.

CAFs supported by analytical techniques such as SEM–EDX have proven to be a versatile and effective tool for monitoring urban air characteristics. Nevertheless, further investigations could focus particularly on some of the characterized parameters. Other analytical techniques can be considered in order to simplify and target the identification of interesting PM such as hazardous pollutants.

Authors' contributions

MGR, BHR and RGS designed the study, supervised data collection and interpretation, MRH, BHR and BRH collected, analyzed, interpreted the data and wrote the draft manuscript. All authors read and approved the final manuscript.

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Competing interests

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.

Availability of data and materials

Data generated during this research work can be available upon request.

Consent to publication

The Author guarantees that the Contribution to the Work has not been previously published elsewhere, or that if it has been published in whole or in part, any permission necessary to publish it in the Work has been obtained and provided.

Ethics approval and consent to participate

The ethical clearance was not required for this particular research because it nether included animal nor plant. This research work did not involve human subject for experimental purpose and informed consent to participate in the study.

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