



Article Particulate Matter Characterization in a Hospital's Underground Car Park

Hector Garcia-Gonzalez^{1,*}, Maida Domat², Teresa Lopez-Pola¹, Pilar Fernandez-Rubio¹ and Pablo Fernandez-Rodriguez¹

- ¹ Instituto Nacional de Silicosis, C/la Minería, 1, 33011 Oviedo, Spain
- ² Department of Physics, University of Oviedo, C/Leopoldo Calvo Sotelo, 18, 33007 Oviedo, Spain

Correspondence: hectorg@ins.es; Tel.: +34-985108009

Abstract: The air quality in a hospital's underground car park is a concern because diesel fumes from cars impact upon vulnerable people attending medical consultations. This research aims to quantify the potential health risk associated with a particular hospital car park. Particulate matter was evaluated in the area with direct reading devices for particle numbers and mass concentrations (CPC 3007, EEPS 3090, Trolex Air XD, Nanozen, and Grimm 1109). Elemental and total carbon concentrations were measured following the NIOSH 5040 method, while volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) were measured through laboratory analysis and Scanning Electron Microscopy and Energy Dispersive using X-Ray Analysis SEM-EDX microscopy. The nanoparticle levels reached over 80,000 nanoparticles/cm³ (double the German Institut für Arbeitsschutz (IFA) benchmark levels). Diesel particulate matter levels measured as elemental carbon were around 35% of the occupational limit, and from the 49 VOCs analyzed only 13 were detected in quantities below the 0.1% of the occupational limit, while levels of the 13 PAHs analyzed, were below the laboratory limit of quantification. The study concludes that particulate matter in the underground car park can easily exceed nanoparticles benchmark levels and could be harmful, mainly to vulnerable people. It is therefore recommended that they use the outdoor car park or minimize their time in the underground one.

Keywords: exposure; ultrafine particles; number concentration; diesel; underground parking

1. Introduction

Characterizing air contaminants in indoor and subsurface facilities is critical to engaging the required measures in order to safeguard vulnerable populations from potentially dangerous sources. Benzene, CO, NO_2 , and, to a lesser extent, other aromatic volatile hydrocarbons and particulate matter are the primary pollutants in areas exposed to motor exhaust emissions [1,2].

In epidemiological studies, short- and long-term urban PM10 and PM2.5 exposure have been linked to morbidity and premature mortality [3]. However, over the last few years, concerns about submicron particles have been increasing. Studies have shown that their surface plays a critical role in their toxic effects, since they have a large surface area to volume ratio compared to the same material in bulk [4,5], greater as the particle size decreases. In addition, they have an almost negligible contribution to the mass of the PM fraction being measured and are therefore often not characterised by the traditional methodologies, which focus on the particle mass concentration.

As regards emissions from diesel engines, it is estimated that around 6% of lung cancer deaths are due to diesel emissions (DE) exposure [6]. They were classified as a group 1 human carcinogen by the IARC (2012) [7], and a specific limit value of 0.05 mg/m^3 will apply in Spain from 21 February 2023 [8]. Therefore, it is necessary to measure the amount



Citation: Garcia-Gonzalez, H.; Domat, M.; Lopez-Pola, T.; Fernandez-Rubio, P.; Fernandez-Rodriguez, P. Particulate Matter Characterization in a Hospital's Underground Car Park. *Powders* **2022**, *1*, 194–206. https:// doi.org/10.3390/powders1040013

Academic Editor: Paul F. Luckham

Received: 19 July 2022 Accepted: 21 September 2022 Published: 30 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and type of DE in the parking areas and consider the available risk management measures so as to stay below the limits.

Diesel particulate matter has a bimodal size distribution: the majority of the particles conforming to DE are within the respirable fraction (PM4), but most of them are ultrafine particles (UFP; 0.100 μ m in diameter or less) [9]. In fact, there is a fraction of DE within the nucleation mode with sizes between 0.03 to 0.030 μ m, and a second fraction from agglomeration mechanisms covering sizes from 0.030 to 0.500 μ m made of solids (elemental carbon 75%, organic carbon 19%, metals and elements 1–4%, sulfate and nitrate 3%) intermixed with other elements, including PAHs and small amounts of other trace elements [10,11].

Previous studies [12,13], identified DE as the primary source of UFPs, showing that direct-reading instruments monitoring Particle Number Concentrations (PNCs) are a more specific way of assessing exposure to DE than the common PM respirable fraction (PM4) or Elementary Carbon (EC).

It has been established that one of the main sources of airborne polycyclic aromatic hydrocarbons (PAHs) in metropolitan areas is vehicle exhaust [14,15], and these PAHs have adverse health effects [16]. It is being reported that there has been an increase in volatile organic compounds (VOCs) emission due to the use of diesel particulate filters in cars [17], and car emissions are an important source of VOCs in urban areas [18].

Although hospital areas are well monitored, the same is not true for the surrounding common areas. Little information is available about the health risks associated with time spent in underground car parks. The underground car park is generally in a closed or semi-closed space, where air pollutants discharged by motor vehicles are hard to diffuse, resulting in poor air quality and potential health risks. Hospital employees and patients are the main users of this type of parking. The former are susceptible to suffering long-term exposure to the air pollutants present in the parking space, while the latter can be classified as vulnerable people attending medical consultations in the hospital.

Therefore, the characterisation of the air pollutants present in an underground hospital parking area was evaluated focusing on the range of UFPs, and as a result, DE, mainly using direct-reading devices and laboratory analysis. Different metrics PNC (Particle number concentrations), PM (Particulate Matter), and PSD (Particle Size Distributions), were compared to each other to assess which ones related most accurately to the results from the laboratory.

2. Materials and Methods

2.1. Characteristics of the Sampling Site

The study was carried out in Oviedo, Asturias, Spain, in the HUCA (Hospital Universitario Central de Asturias) car park 1, which is located 2.5 km from the City centre, in the North West, in an area with residential buildings and a shopping centre, and which has communications with two nearby highways.

The car park is located on the side of the hospital building. Pedestrian access to the parking is provided via four stairwells and two elevators. There are 722 parking spaces and 22 motorcycle spaces distributed on two floors, each of 9643 square meters. The first floor provides access from one side and has natural ventilation, while the second floor is fully underground (Figure 1).

More than 1000 cars use the car park daily from Monday to Friday. When hospital activity is reduced on weekends and holidays, the number of vehicles is much less. Before the COVID-19 pandemic, the car park was used by about 20,000 cars on average per month; since then, the monthly average has dropped to around 15,000 vehicles. On the one hand, the transit of patients was reduced since hospital appointments only allowed one person each time. Thus, many people travelled alone by public transport or were brought by a driver who did not have to park. Visits to hospitalised patients were also restrained to one person and at specific time slots. Therefore, the distribution of parking visits was also different than it had been previously. One of the three parking areas was closed due to the



Figure 1. Parking garage layout Level -2, and aerial photography.

The outdoor air quality in the station nearby the parking fulfils the legislation: in 2021, only ten days exceeded the regulated 50 μ g/m³ for PM10 although the PM10 annual average was 23 μ g/m³ and the PM2.5 annual average 13 μ g/m³ [19].

All the measurements were carried out in level -2, following the safety criteria of the worst-case scenario [20]. Data were collected continuously from 15 November to 3 December 2021 with the Trolex Air XD on several alternative days with EEPS 3090, CPC 3007, Nanozen, and GRIMM 1109.

2.2. *Sampling Methodology*

2.2.1. Particle Sampling

To obtain real-time information, different direct reading devices were in place. Measuring metrics and particle size ranges were different for each device, covering a wide range, from 0.0056 μ m to 34 μ m. PNCs were measured with a Condensation Particle Counter CPC 3007, while PM was measured with Trolex Air XD, Nanozen, and Grimm 1109, and Particle Size Distributions (PSDs) were measured with an Engine Exhaust Particle Sizer EEPS 3090 and Grimm 1109. A summary of the measuring ranges and specifications of each of the devices can be seen in Table 1.

Having different metrics to detect the airborne particles ensures the coverage of the whole range of sizes, since UFPs have a very low impact in mass but are present in high PNCs, and the opposite occurs for particles greater than a micron (high PM, low PNC). Therefore, instruments covering both types of metrics are necessary, especially when a particular material such as DE is to be detected and it is not clear which range will show the greatest concentration of particles.

The CO is monitored by an internal system situated in the car park. This system activates the mechanical ventilation as follows; when CO levels reach 50 ppm, one extraction system starts; when achieving 100 ppm, a second one starts, and if it exceeds 150 ppm, the emergency mode is initiated.

Before sampling, instruments were calibrated according to the manufacturer's instructions, and "zeroing" was done every day before sampling. After sampling, filters were changed, slits cleaned daily, and batteries were replaced to ensure reproducibility and comparability among samples from different days. All the nozzles of the devices

Instrument Sampling Principle Main Metric Range CPC 3007 (TSI Inc., 0.010 to 1 μm Condensation nuclei counter Particle number concentration 10⁵ particles/cm³ Shoreview, MN, USA) **EEPS 3090 Engine Exhaust Particle** Ultrafine particle size 0.0056 to 0.56 µm (TSI Inc., Sizer Spectrometer distribution (nanoparticles) 32 Channels Shoreview, MN, USA) Nanozen **Optical Particle** Particle mass concentration PM4 (0.3 to 4.3 µm (Nanozen industries Inc., Counter (OPC) and size distribution 12 Channels) Vancouver, BC, Canada) PM10, PM4, PM2.5, PM1 Trolex Air XD **Optical Particle** Particle mass concentration (Trolex Ltd., Hazel Grove, UK) Counter (OPC) and size distribution (24 Channels) **GRIMM 1109** 0.0265 to 34 µm (Grimm Durag Group, Particle size distribution Spectrometer 32 Channels Hamburg, Germany)

(Figure 1).

Table 1. Direct reading instruments used for monitoring the particulate fraction.

were pointing towards the East, which is the entrance for cars coming from the first floor

2.2.2. Diesel Particulate Matter (as Elemental Carbon)

Diesel particulate matter was sampled and analyzed following the NIOSH 5040 [21] methodology. A personal Apex 2 pump was calibrated to 2 L/min, a tygon tube, and a 3-piece cassette were used. The sample was collected in a 37 mm quartz fibre filter (previously cleaned in a muffle furnace at 800 °C for 1 h) with the support of a cellulose pad. The sampler flow rate was checked before each sampling using a calibrated MesaLabs-Bios-DryCal-Defender 530 and adjusted if necessary so that it was within 0.010 L/min of the target value. It was also checked after the sample was taken. The sampling duration was 346 min.

After collecting the sample, the filters were sent to the laboratory and analyzed with an Organic Carbon/Elemental Carbon Analyser (OCEC). In order to completely remove all organic carbon and turn it into carbon dioxide, samples were heated over four temperature ramps. The flame ionization detector (FID) was used to detect the methane that results from the reduction of this carbon dioxide. The calibration of a given amount of carbon was then done using known amounts of methane. The amount of organic and elemental carbon in a sample can be calculated using the laser transmission data, the response from the FID detector, and other information. The detection limits for elemental and organic carbon (OC) are 1 to 15 g per cm² and 5 to 400 g per cm², respectively. For OC and EC, lower detection limits are in the range of 0.2 g per cm² of a filter.

The working range for elemental and organic carbon are 0.5 to 100 μ g per cm² and 2 to 100 μ g per cm², respectively. For OC and EC, lower detection limits are in the range of 0.2 μ g per cm² of a filter.

2.2.3. Volatile Organic Compounds (VOCs)

VOCs were sampled with a personal pump, a Tygon tubing air sampling, and a Tenax[®] TA sorbent tube (Markes International Ltd., Bridgend, Wales, UK).

The pump selected was the Gil Air Plus; the pump is designed to provide a stable, controlled flow rate of approximately 20 to 5100 cc/min. All the pumps used were annually maintained to avoid pulsations and fluctuations in the flow rate.

The sampler flow rate was checked and adjusted to (50 mL/min) before each sampling using a calibrated MesaLabs Bios DryCal Defender 530. It was also checked after the test was complete. The sampling time selected was 100 min. Once sampling was completed, the Tenax[®] TA sorbent tube was refrigerated (temperature between 0 to 5 °C) and sent to the laboratory for analysis. The laboratory analyzed 49 different VOCs. The limit of quantitation (LOQ) for VOCs is 0.1 ng. A Gas Chromatograph (Agilent 5975 C), a thermal desorption

(MARKES UNITY 2), an HP-INNOWax Column, and ancillary elements were used. The procedure analyses 49 VOCs (Hexane, 2,4-Dimethylpentane, Isooctane, n-Heptane, n-Octane, Carbon tetrachloride, 1,1,1-Trichloroethane, n-Nonane, Ethyl acetate, 2-Butanone, Benzene, n-Dean, Trichlorethylene, 4-methyl-2-pentanone, Pinene, Tetrachloroethylene, Chloroform, Toluene, 1,2-dichloropropane, 1,2-Dichloroethane, N-butyl acetate, n-Undecano, b-Pinene, Ethylbenzene, p-Xylene, m-Xylene, n-Butanol, Bromodichloromethane, n-Dodecane, o-Xylene, d-Limonene, Propilbenzene, 2-Ethiltoluene, 3-Ethiltolueno, 1,3,5-Trimethylbenzene, Styrene, 4-Ethyltoluene, n-Tridecane, 1,2,4-Trimethylbenzene, Dibromochloromethane, 1,2,3-Trimetilbenceno, n-Tetradecane, Nonanal, 1,2,4,5-Tetramethylbenzene, 1,4-Dichlorobenzene, n-Pentadecane, Decanal, n-Hexadecane, Naphthalene).

2.2.4. Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs were sampled with a Sven Leckel Low Volume Sampler (LVS3) calibrated at 2.3 m³/h with a PM10 inlet. The sample was collected in 47 quartz filters for 24 h. Once collected, the samples were refrigerated and sent to the laboratory for analysis with a gas chromatograph Shimazu GC-2010 Plus and a Shimazu GCMS-QP2010 Ultra. The laboratory analysed 17 different PAHs (Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(ghi)perylene).

2.2.5. Characterization with SEM-EDX Microscopy

Particulate matter was also collected with a Sven Leckel Low Volume Sampler (LVS3) calibrated at 2.3 m³/h with a PM10 inlet and 47 mm PVC filters, and two SKC Leland Legacy high flow pumps, one calibrated at 10 L/min with an FSP-10 cyclone and 37 mm PVC filter (PM4) and the other one calibrated at 14 L/min with a GK 2.69 cyclone and polycarbonate (PC) filter (PM1). The three selected filters characterized by electronic microscopy had the following volumes: the 37 mm PC filter which collected PM1 material had a volume of 3275 L, the 37 mm PVC collecting PM4 had a volume of 2359.9 litres and a 47 mm PVC for PM10 had a volume of 55,200 litres.

Filters were metallized with gold and analyzed in a Scanning Electron Microscopy SEM (JEOL JSM-5600, JEOL Ltd., Tokyo, Japan) with built-in EDX-microanalysis. Particle size, state of aggregation/agglomeration and elemental composition were analyzed.

2.3. Limits

In Spain, Occupational Exposure Limits (OEL) are provided by the Instituto Nacional de Seguridad e Higiene en el Trabajo (INSST), [22]. Nevertheless, when any of the chemicals analyzed is a carcinogen, the exposure levels must be as low as technically possible [23,24].

2.3.1. Particle Number Concentrations

A safe UFPs exposure is still debatable, and there are no standard measurement techniques or instruments; which results in the fact that there are currently no air quality regulations to control exposure to airborne nanoparticles. Nonetheless, the surface of nanoparticles plays a critical role in their toxic effects. Particle concentrations in the environment (based on number or surface) are a better metric for assessing risks of fine particles and UFP's than the mass-based approach that has been used in the past (and is still used officially). UFP's have a large surface area to volume ratio compared to the same material in bulk [4,5].

Because there are numerous nanoparticles with varying sizes and heterogeneous compositions, the German Institut für Arbeitsschutz proposed a benchmark concentration level based on the PNC instead of the classic and official approach based on the mass concentration, Table 2.

Description	Density	Benchmark Level (8-h Time-Weighted Average (TWA))
Biopersistent granular nanomaterial in the range 1–100 nm	>6000 kg/m ³	20,000 particles/cm ³
Biopersistent granular nanomaterial in the range 1–100 nm	$< 6000 \text{ kg/m}^3$	40,000 particles/cm ³
Non-bio-persistent nanomaterial in the range 1–100 nm		Applicable OEL

Table 2. Nano reference values, based on the benchmark level (IFA, 2009) [25].

The OEL for respirable dust PM4 is 3 mg/m³ [22], while the legislation for environmental air quality allows up to 50 μ g/m³ (daily outdoors) for PM10, up to 25 μ g/m³ (annual average, outdoors) for PM2.5 and up to 20 μ g/m³ for PM2.5 indoor air quality. The World Health Organization (WHO) recommended level for PM10 is 40 μ g/m³ (24 h), and 15 μ g/m³ (annual average), while for PM2.5 a maximum of 20 μ g/m³ (24 h) is recommended [26]. There is a mass-based approach with similar legislation in most countries.

2.3.2. Diesel Particulate Matter (as Elemental Carbon)

Although having in place direct reading instruments to collect the PNC of UFPs (and thus, the fraction of DE falling within this range), elemental carbon (EC) is recommended as a measure of exposure to DE [21] and will be used as a reference for comparison. Organic carbon (OC) is not preferred since other interfering elements may be present.

Since an OEL of 0.05 mg/m^3 , measured as elemental carbon, will be applied from 21 February 2023 [8,23], this will be the limit value taken as a reference for this study.

2.3.3. Volatile Organic Compounds (VOCs)

Table 3 shows the OEL for several VOCs. Regarding the environmental values, Total Volatile Organic Compounds (TVOC) are generally analyzed [27]. The recommended value of TVOC for an indoor environment is $200 \ \mu g/m^3$ [28,29].

VOCs	OEL (mg/m ³)
n-Heptane	2085
n-Octane	1420
n-Nonane	1065
Benzene	3.25
1,2-dichloropropane	47
p-Xylene	221
n-Butanol	61
o-Xylene	221
1,3,5-Trimethylbenzene	100
Styrene	86
1,2,4-Trimethylbenzene	100
1,2,3-Trimethylbenzene	100

Table 3. The occupational limit for VOCs INSST [22].

Nevertheless, some VOCs have no recommended safe level for being a carcinogen and the exposure should be as low as possible. Table 4 shows the Public Health England guide for indoor VOCs benchmark levels.

Noc	Limit Values in µg/m ³			
vocs –	Short Term	Long Term	- Source	
Acetaldehyde (75-07-0)	1420 (1 h)	280 (1 day)	Health Canada (2018)	
α-Pinene (80-56-8)	45,000 (30 min)	4500 (1 day)	EPHECT (Trantallidi et al., 2015)	
Benzene (71-43-2)	No recommended level of exposure		World Health Organisation (2010)	
D-Limonene (5989-27-5)	90,000 (30 min)	9000 (1 day)	EPHECT (Trantallidi et al., 2015)	
Formaldehyde (50-00-0)	100 (30 min)	10 (1 year)	World Health Organisation (2010)	
Naphthalene (91-20-3)	-	3 (1 year)	Agency for Toxic Substances & Disease Registry (2005), USA	
Styrene (100-42-5)	-	850 (1 year)	Health Canada (2018)	
Tetrachloroethylene (127-18-4)	-	40 (1 day)	Health Canada (2018)	
Toluene (108-88-3)	15,000 (8 h)	2300 (1 day)	Health Canada (2018)	
Trichloroethylene (71-01-06)	No recommended level of exposure		World Health Organisation (2010)	
Xylenes-mixture (1330-20-7)	-	100 (1 year)	Health Canada (2018)	

Table 4. Indoor air quality guidelines for selected VOCs [30].

2.3.4. Polycyclic Aromatic Hydrocarbons (PAHs)

From the 17 polycyclic aromatic hydrocarbons (PAHs) analyzed, only naphthalene has an occupational limit OEL of 53 mg/m^3 [22].

The International Agency for Research on Cancer (IARC) classified the Benzo(a)pyrene as carcinogenic to humans (Group 1), and Dibenzo(a,h)anthracene as probably carcinogenic to humans (Group 2A). Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Chrysene, Indeno (1,2,3-cd)pyrene are classified as possibly carcinogenic to humans (Group 2B) [31].

3. Results and Discussion

3.1. Particles and Ultrafineparticles

On a typical day, cars start arriving at around 7:30 a.m., and the car park is full within a few hours. There is a steady stream of vehicles throughout the day, mostly belonging to patients, until around 2:30 p.m., when employees begin to leave.

Table 5 shows the result for PM10, PM4, PM2.5, and PM1 with the Trolex Air XD and the Nanozen. The concentrations for those particle mass fractions are well below the legal levels, increasing on average during rush hours. The right side of Figure 2 plots this data statistically, showing an apparent deviation to higher mass concentrations as the particle size range increases due to the contribution of coarse particles, not only in mass but also in diameter.

Device	Sampling Time	PM1 (μg/m ³)	PM 2.5 (μg/m ³)	PM 4 (μg/m ³)	PM 10 (μg/m ³)
Trolex Air XD	Average (24 h)	2.21	6.29	9.90	16.02
Trolex Air XD	Average (8:00 to 15:00)	2.49	7.45	12.30	21.16
Nanozen	Average (8:00 to 15:00)	-	-	7.1	-

Table 5. Particulate Matter Values for the underground parking spot.

The left side of Figure 2 represents PM1 concentrations for 24 h on a working day. It can be seen that the concentration remains steady the whole day and night, with a slight increase in the morning starting at 8:00 a.m. until 6:00 pm, corresponding to the full working period. This is also reflected in the right plot of Figure 2, where the mean and median in this particle range are similar since particles in the UFP barely contribute to the mass concentration.



Figure 2. Left: PM1 concentration on a working day. **Right**: Data from particulate matter summarized in Table 5 represented statistically.

Regarding PNCs levels recorded with the CPC and EPPS (Figure 3), concentration of 80,000 particles/cm³ was monitored in the car park on a working day, and the concentration remained almost stable, the spike peaks being caused by vehicles passing near the instrument.



Figure 3. Left: Example of ultrafine PNC evolution in the parking area (from CPC 3007). **Right**: ultrafine PSD (from EEPS 3090).

According to Table 2, this high concentration of ultrafine particles is double the benchmark level and may be potentially dangerous to health. In the right part Figure 3, it can be seen that the majority of particles of this concentration are below 0.2 μ m, with two modes at around 0.015 μ m and 0.070 μ m, confirming the idea that the broadest contribution from the air pollutants coming from the motor exhaust is within this UFP range. Further comparison of the constituents of these samples will demonstrate whether DE is exceeding the safe limits.

However, although the Grimm 1109 instrument shows a PSD (Figure 4—Left) where the majority of particles lay below 0.3 μ m, there is another mode around 2 μ m. The time evolution of one of these samples from particles between 0.265 and 0.615 μ m (Figure 4—Right) shows a constant contribution of particles from 10:30 am to 1:50 pm, peaking at around 1:30 pm, the starting time of the lunch break in Spain. PNC decreases with increasing size. Although the Grimm 1109 instrument can measure sizes from 0.265 μ m to 34 μ m in 32 channels, only contributions greater than 10 particles/cm³ were plotted in Figure 4 for clarity. Therefore, it can be seen that the number of particles above 10 μ m is negligible.



Figure 4. PSD (left) and PNC (right) time evolution between 0.265 and 0.615 µm from Grimm 1109.

In order to get a clearer image of the PM distribution in the parking area, Figure 5—Left shows the average mass concentration using the Grimm 1109. What is remarkable, is that there is a large percentage of particles below 0.400 μ m, which are normally present in large numbers but have much less mass compared with coarser particles. In this case, there is a clear peak of particles between 3 to 15 μ m, peaking at the range of between 4 to 6 μ m, although some of the mass values reached are comparable to the ones achieved by particles between 0.265 μ m (the lower limit of the instrument) and 0.400 μ m. This fact indicates a large concentration of particles in the fine range, as is shown in Figure 4.





The PM evolution with time (Figure 5—Right) shows a behaviour analogous to Figure 4—Right, where the concentration was constant with time except for the peak during the lunch break and decreased with increasing size for particles below $0.615 \mu m$.

3.2. Diesel Particulate Matter (as Elemental Carbon)

The first sample had 0.022 mg/m³ Elemental Carbon (EC), 0.063 mg/m³ Organic carbon (OC) and 0.085 mg/m³ Total carbon (TC). The second sample had 0.013 mg/m³ (EC), 0.069 mg/m³ (OC), and 0.085 mg/m³ (TC). Both samples are below the limit value proposed for 2023.

3.3. Volatile Organic Compounds (VOCs)

Table 6 shows the 13 VOCs detected in the hospital parking. The other 36 VOCs were in quantities below the laboratory limit of detection.

Table 6. Shows the 13 VOCs detected in the hospital park	ing.
--	------

VOCs	μg/m ³	
n-Heptane	2.73	
Benzene	2.5	
Ethylbenzene	2.44	
p-Xylene	1.4	
m-Xylene	2.32	
n-Dodecane	0.61	
o-Xylene	2.32	
1,3,5-Trimethylbenzene	0.79	
Styrene	1.05	
n-Tridecane	1.83	
1,2,4-Trimethylbenzene	3	
n-Pentadecane	1.8	
n-Hexadecane	1.07	

3.4. Polycyclic Aromatic Hydrocarbons (PAHs)

The 17 different PAHs analyzed in five samples were all below the laboratory detection limit.

3.5. SEM-EDX Microscopy

In the PC filter collecting PM1 (Figure 6—Left), only a few coarse agglomerates or particles were found, carbon and oxygen being the main components in their composition, together with traces of Silica and other metals such as Mg, Al, Fe in portions ranging from 2–10%.

In the PVC filters multiple clusters of regular nanoparticles of sizes between 30–60 nm were found. Although the characterization of such nanoparticles was not easy because of the EDX resolution, it was found that the main elements detected in the PVC filter, collecting PM4 (Figure 6—Center), were: carbon (55% average), oxygen (15% average), chlorine (13% average) and metals such as Na, Al, Ca, Fe, Cu, Zn in rates below 1.5% on average, except for the iron, which had a presence of over 5%.

In the PVC filter collecting PM10 (Figure 6—Right), carbon and oxygen were identified at the same rates as the previous PVC filter, but only silica and iron (10% average each) were found.



Figure 6. Left: PC filter (37 mm, PM1); Center: PVC filter (37 mm, PM4); Right: PVC filter (47 mm, PM10).

4. Conclusions

Particulate matter levels were evaluated using direct-reading devices in a hospital underground parking facility. Although there is still no legislation in Spain regarding the levels of nanoparticles, according to the German reference levels (IFA, 2009), for amounts more significant than 40,000 particles/cm³, there may be a health risk. In the hospital car park, an average of 80,000 particles/cm³ was found with two modes at the UFP size range of 0.015 μ m and 0.070 μ m.

The classic (and official) mass concentration average approach states a value of 3 mg/m^3 for occupational respirable dust levels. Compared with this, the average respirable dust levels measured in the car park PM4 (12.3 µg/m³), stands out as a much lower value. The PM2.5 levels in the car park (6.29 µg/m³ 24 h) are also below the WHO recommendation ($20 \mu g/m^3 24 h$). However, the UFPs' concentration is double the benchmark level, which indicates a potential risk. Since most of the fraction of the diesel fumes, a group 1 human carcinogen substance, falls into the UFP size region, and will soon be regulated, it was also monitored. Diesel particulate matter levels measured as elemental carbon were found at around 35% of the OEL. From the 49 VOCs analyzed, only 13 were detected in quantities below 0.1% of the OEL. Nevertheless, some of the VOCs are classified as carcinogenic substances, and the exposure levels must be as low as is technically possible. The 17 different PAHs analyzed in five samples were all below the laboratory detection limit. Microscopy characterization detected large amounts of agglomerates of UFPs, mostly made of carbon, silica, chloride and metals, in proportions that could confirm that some of them belong to DE.

Even though the levels of all pollutants analyzed were well within current legislation standards for air quality, it is recommended that people spend the minimum amount of time possible in the car park and avoid using the car park as a waiting area. It is also recommended with some urgency, that the ventilation system be improved, not only when the CO levels are exceeded, but also by placing a fine or ultrafine particle monitoring system for activating ventilation systems when exceeding the benchmark level. Other additional measures that can be considered are allowing only cars with eco-stickers O, Eco, B & C in the underground car park (vehicles with low emissions).

Author Contributions: Conceptualization, H.G.-G.; methodology, H.G.-G., M.D. and T.L.-P.; validation, all; formal analysis, all; investigation, all; data curation, M.D. and H.G.-G.; writing—original draft preparation, H.G.-G. and M.D.; writing—review and editing, all; laboratory chemical analysis, P.F.-R. (Pilar Fernandez-Rubio) and P.F.-R. (Pablo Fernandez-Rodriguez). All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: This paper and the research behind it would not have been possible without the exceptional support from the Instituto Nacional de Silicosis and the University of Oviedo. We would also like to express our gratitude to the HUCA library for all the reference material and information provided, the University of Oviedo Servicios Científico-Técnicos for the technical support provided with the SEM-EDX microscopy analysis, and GISPASA for supplying data from the parking.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Glorennec, P.; Bonvallot, N.; Mandin, C.; Goupil, G.; Pernelet-Joly, V.; Millet, M.; Filleul, L.; Le Moullec, Y.; Alary, R. Is a quantitative risk assessment of air quality in underground parking garages possible? *Indoor Air* 2008, 18, 283–292. [CrossRef] [PubMed]
- Hwang, S.H.; Park, W.M. Indoor air quality assessment with respect to culturable airborne bacteria, total volatile organic compounds, formaldehyde, PM₁₀, CO₂, NO₂, and O₃ in underground subway stations and parking lots. *Air Qual. Atmos. Health* 2019, 12, 435–441. [CrossRef]
- Violante, F.S.; Barbieri, A.; Curti, S.; Sanguinetti, G.; Graziosi, F.; Mattioli, S. Urban atmospheric pollution: Personal exposure versus fixed monitoring station measurements. *Chemosphere* 2006, 64, 1722–1729. [CrossRef] [PubMed]

- 4. Van Veelen, W.; Streekstra, W.-H.; Van Broekhuizen, P.; Schulte, P.; Reijnders, L. Exposure Limits for Nanoparticles: Report of an International Workshop on Nano Reference Values. *Ann. Occup. Hyg.* **2012**, *56*, 515–524. [CrossRef]
- Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT) Seguridad y salud en el trabajo con Nanomateriales. 2015. Available online: https://www.insst.es/documentacion/catalogo-de-publicaciones/seguridad-y-salud-en-el-trabajo-connanomateriales (accessed on 26 April 2022).
- Vermeulen, R.; Silverman, D.T.; Garshick, E.; Vlaanderen, J.; Portengen, L.; Steenland, K. Exposure-Response Estimates for Diesel Engine Exhaust and Lung Cancer Mortality Based on Data from Three Occupational Cohorts. *Environ. Health Perspect.* 2014, 122, 172–177. [CrossRef] [PubMed]
- IARC Diesel Engine Exhaust Carcinogenic. 2012. Available online: https://www.iarc.who.int/wp-content/uploads/2018/07/ pr213_E.pdf (accessed on 26 April 2022).
- 8. Directive 2004/37/EC—Carcinogens or Mutagens at Work | Safety and Health at Work EU-OSHA. Available online: https://osha.europa.eu/en/legislation/directive/directive-200437ec-carcinogens-or-mutagens-work (accessed on 31 March 2022).
- Debia, M.; Neesham-Grenon, E.; Mudaheranwa, O.C.; Ragettli, M.S. Diesel exhaust exposures in port workers. J. Occup. Environ. Hyg. 2016, 13, 549–557. [CrossRef] [PubMed]
- 10. Wichmann, H.-E. Diesel Exhaust Particles. Inhal. Toxicol. 2007, 19, 241–244. [CrossRef] [PubMed]
- Kittelson, D.; Watts, W.; Johnson, J.; Air, C.; Board, R. Engine Manufacturers Association (EMA) South Coast Air Quality Management District. Available online: https://www.oyez.org/cases/2003/02-1343 (accessed on 26 April 2022).
- 12. Debia, M.; Trachy-Bourget, M.-C.; Beaudry, C.; Neesham-Grenon, E.; Perron, S.; Lapointe, C. Characterization of indoor diesel exhaust emissions from the parking garage of a school. *Environ. Sci. Pollut. Res.* **2016**, *24*, 4655–4665. [CrossRef] [PubMed]
- Cantrel, B.K.; Rubow, K.L.; Watts, W.F., Jr.; Bagley, S.T.; Carlson, D.H. Pollutant Levels in Underground Coal Mines Using Diesel Equipment. In Proceedings of the 6th US Mine Ventilation Symposium, Salt Lake City, UT, USA, 21–23 June 1993.
- Li, H.; Zeng, X.; Zhang, D.; Chen, P.; Yu, Z.; Sheng, G.; Fu, J.; Peng, P. Occurrence and carcinogenic potential of airborne polycyclic aromatic hydrocarbons in some large-scale enclosed/semi-enclosed vehicle parking areas. *J. Hazard. Mater.* 2014, 274, 279–286. [CrossRef] [PubMed]
- 15. Ravindra, K.; Sokhi, R.; Van Grieken, R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* **2008**, *42*, 2895–2921. [CrossRef]
- Ravindra, K.; Bencs, L.; Wauters, E.; de Hoog, J.; Deutsch, F.; Roekens, E.; Bleux, N.; Berghmans, P.; Van Grieken, R. Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. *Atmos. Environ.* 2006, 40, 771–785. [CrossRef]
- 17. Qian, F.; Xue, C.-X.; Xu, X.-W.; Ma, D.; Li, P.; Zhu, N. VOCs Emission Characteristics of DPF Regeneration in National VI Diesel Engine. *Huan Jing Ke Xue* 2020, *41*, 674–681. [PubMed]
- Wang, S.; Yuan, B.; Wu, C.; Wang, C.; Li, T.; He, X.; Huangfu, Y.; Qi, J.; Li, X.; Zheng, J.; et al. Oxygenated VOCs as Significant but Varied Contributors to VOC Emissions from Vehicles. *Atmos. Chem. Phys. Discuss.* 2022, 22, 9703–9720. [CrossRef]
- 19. Government of the Principality of Asturias. Air Quality in Asturias 2021. 2022. Available online: https://cutt.ly/FZoqEJL (accessed on 28 May 2022).
- U.S. EPA. Guidelines for Exposure Assessment. EPA/600/Z-92/001. 1992. Available online: https://www.epa.gov/sites/ default/files/2014-11/documents/guidelines_exp_assessment.pdf (accessed on 26 April 2022).
- NIOSH Diesel Particulate Matter (as Elemental Carbon) 5040. Available online: https://www.cdc.gov/niosh/docs/2003-154 /pdfs/5040.pdf (accessed on 26 April 2022).
- Límites de Exposición Profesional para Agentes Químicos 2022—Portal INSST-INSST. Available online: https://www.insst.es/ documentacion/catalogo-de-Publicaciones/limites-de-exposicion-profesional-para-agentes-quimicos-2022 (accessed on 26 April 2022).
- Ministerio de la Presidencia of Spain. Royal Decree 665/1997 on the Protection of Workers from the Risks Related to Exposure to Carcinogens at Work (1997, Updated on June 2021). Available online: https://www.boe.es/buscar/act.php?id=BOE-A-1997-111 45 (accessed on 26 April 2022).
- Gonzalez, H.G.; García-Ordiales, E.; Diez, R.R. Analysis of the airborne mercury and particulate arsenic levels close to an abandoned waste dump and buildings of a mercury mine and the potential risk of atmospheric pollution. SN Appl. Sci. 2022, 4, 76. [CrossRef]
- Deutsche Gesetzliche Unfallversicherung, D.G.U. IFA—Technical Information: Ultrafine Aerosols and Nanoparticles at the Workplace. Available online: https://www.dguv.de/ifa/fachinfos/nanopartikel-am-arbeitsplatz/beurteilung-vonschutzmassnahmen/index-2.jsp (accessed on 22 June 2022).
- 26. World Health Organization. WHO Global Air Quality Guidelines. Particulate Matter (PM2.5 and PM10), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide; World Health Organization: Geneva, Switzerland, 2021; ISBN 9789240034228.
- 27. García, H.; Pola, T.L. Health and safety in 3D printing. Int. J. Occup. Environ. Saf. 2022, 6, 14–25. [CrossRef]
- Mečiarová, Ľ.; Vilčeková, S.; Burdová, E.K.; Kiselák, J. Factors Effecting the Total Volatile Organic Compound (TVOC) Concentrations in Slovak Households. Int. J. Environ. Res. Public Health 2017, 14, 1443. [CrossRef] [PubMed]
- Working group 13 Total Volatile Organic Compounds (TVOC) in Indoor Air Quality Investigations; European Collaborative Action, Indoor Air Quality & Its Impact on Man. 1997. Available online: https://cdn.sparkfun.com/assets/learn_tutorials/1/4/ 3/ECA_Report19.pdf (accessed on 26 April 2022).

- Public Health England. Public Health England Indoor Air Quality Guidelines for Selected Volatile Organic Compounds (VOCs) in the UK; Public Health England: London, UK, 2019; p. 9. Available online: https://assets.publishing.service.gov.uk/government/uploads/ system/uploads/attachment_data/file/831319/VO_statement_Final_12092019_CS_1_.pdf (accessed on 26 April 2022).
- 31. IARC. Chemical Agents and Related Occupations; IARC: Lyon, France, 2012; ISBN 978-92-832-1323-9.