

# CONTRIBUTION OF BRAKE EMIS<mark>SIONS</mark> TO MEASURED EXPOSURE AT SPECIFIC, CLOSED DEMO SITES DERIVED

## WP3, TASK3.2

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DoA	Task 3.2. Exposure level will be measured at demonstration sites such as bus stops, tunnels and metro stations and in at least two different seasons. The specific positioning for setting up measurements will be discussed with local partners. Scientific- grade instruments like cyclones, OPC, FMPS, CPC will be selected for time-resolved measurements of PM10, PM2.5, PM4, PM1, and also PN. Low-cost sensors and higher-ranked ones like Dr. Födisch FDS15, TSI dust track, Palas Fidas Frog will be used for longer duration and spatial distribution measurements. Daily PM2.5 filter		





samples will be obtained for inorganic chemical analysis (trace metals) using a high-volume sampler. In addition, CO<sub>2</sub> (for number of passengers) and environmental data like temperature and humidity will be obtained at each location. Measurements will be carried out by local teams, e.g. CARTIF at Valladolid, but supervised by CSIC to ensure quality of data and processing. The effect of environmental conditions and influences such as wind, outdoor air quality, people and traffic will be assessed.

DATE	VERSION	AUTHOR	COMMENT
2023/12/01	1	Teresa Moreno	First draft of deliverable
2023/12/22	2	Teresa Moreno	Final draft of deliverable
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senschaft Federal Department of Economic Education and Research EAER State Secretariat for Education, Research and Innovation SERI Figure 15 Comparison between mass concentrations of organic carbon (OC), rock-forming mineral dust (Mineral), and total PM2.5. In most cases, peaks define similar broad patterns, although there are some exceptions, such as the prominent mineral dust peak on 6th June.

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Figure 17 Multi-element time series plot showing variations in the daily average concentrations of 9 metals present within ambient air of the AUVASA bus depot throughout the monitoring campaign. Five peaks are evident, defined most clearly by Fe and Zn concentrations. See text for details.







## LIST OF ABBREVIATIONS

ACRONYM	DESCRIPTION
AQ	Air Quality
As	Arsenic
AUVASA	Autobuses Urbanos de Valladolid, S. A.
AVa	Ayuntamiento de Valladolid
Ва	Barium
BC	Black Carbon
BDPF	Brake Dust Particle Filter
Bi	Bismuth
BL	Base levels
CARTIF	Centro tecnologico CARTIF
CNG	Compressed Natural Gas
Со	Cobalt
СРС	Condensation Particle Counter
Cr	Chromium
CSIC	Consejo Superior de Investigaciones Cientificas (Spanish Research Council)
Cu	Copper
EC	Elemental Carbon
Fe	Iron
Ge	Germanium
Hf	Hafnium
HREE	Heavy Rare Earth Elements



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HVS	High Volume Sampler
IUTA	Institut für Energie und Umwelttechnik e.V.
LPG	Liquid Petroleum Gases
Metro Lisbon	Metropolitano de Lisboa EP
M+H	MANN+HUMMEL GmbH
Mn	Manganese
NFA	Det Nationale Forskningscenter Forarbejdsmiljo
Ni	Nickel
OC	Organic Carbon
OPC	Optical Particle Counter
PM (PM2.5, PM10)	Particulate Matter (smaller than 2,5 microns, smaller than 10 microns)
PMF	Positive Matrix Factorization
S	Sulphur
Sb	Antimony
Sc	Scandium
SDA	Sofia Development Association
SMPS	Scanning Mobility Particle Sizer
Sn	Tin
Sr	Strontium
Th	Thorium
Ti	Titanium
Ti V	Titanium Vanadium
Ti V W	Titanium Vanadium Tungsten







# LIST OF SYMBOLS

SYMBOL	DESCRIPTION
μg/m³	Micrograms per cubic metre
ng/m <sup>3</sup>	Nanograms per cubic metre







## PUBLISHABLE SUMMARY

This deliverable is related to Task 3.2 and involves measuring the background ("baseline") levels of air quality (AQ) for users and workers at a specific, closed monitoring site, and investigating the likely presence of brake particles in the ambient air. The deliverable has been led by CSIC, with contributions from M+H, CARTIF and AUVASA.

Within this task the exposure levels of air pollutants are being measured at semi-indoor demonstration sites such as bus transportation depots and metro stations using monitoring equipment such as Optical Particle Counter (OPC), Dust Track and low-cost sensors. These instruments provide data on the concentration levels of main pollutants such as inhalable particulate matter (PM), however, to investigate the contribution of specific airborne particle sources, such as brake wear and its associated trace metals, the chemical composition of PM is needed. To get such data, it is necessary to collect PM2.5 filter samples for inorganic chemical analysis using a high-volume sampler. As of November 2023, one AeroSolfd full project campaign has been completed in the AUVASA bus depot at Valladolid, Spain, and physicochemical data successfully obtained and analysed. Based on these data, we present our investigation of baseline air pollutant levels and daily variations in PM chemistry, focussing especially on the trace metals likely to indicate the presence of brake-sourced airborne particles in this semi-enclosed public transport location. A campaign in the Lisbon metro subway is currently in process, and a second campaign in AUVASA bus depot is planned for the first half of 2024. This latter campaign will result in a doubling of the number of PM chemical analyses, thus creating a database numerically large enough to undertake a more sophisticated source apportionment analysis regarding the contribution of brake particles to the air in this location. This will enhance the initial observations and conclusions presented in this current document.

The key questions to be addressed in this work package are (1) what is the air quality (AQ) within semienclosed transport-related working microenvironments and why does it vary? (2) can metalliferous emissions from non-exhaust sources such as brakes and tyres be recognised in the AQ data? (3) what can be done to improve AQ and thus benefit the workers? In this deliverable, we report on AQ inside the AUVASA bus depot in Valladolid, Spain. Our results show that (1) daily AQ inside the bus depot is highly variable; (2) ambient inhalable particle mass concentrations are usually higher at the start of the working day soon after 07.00, when a "rush hour" bus traffic peak is common; (3) peaks in ambient PM concentrations are common during the night/early morning, probably due at least in part to emissions released during maintenance work; (4) the presence of inhalable particles released from brakes is strongly suggested by close correlations between classic "brake-related" elements, notably Fe, Cu, Sb, Cr and, to a lesser extent, Ba; (5) the presence of particles released from tyres is suggested by transient peaks in the concentration of Zn but no other metals; (6) improvements in ventilation and/or use of air purifiers, especially during rush hour peaks and when maintenance work is being performed, are the most obvious ways to improve AQ in the working environment for the depot employees.

The main consumers for this deliverable, i.e. who should read it, include not only those specifically working in the bus depot monitoring site but also all employees working in similar semi-enclosed transport-related micro-environments. Our recommendations for follow-up actions within the AeroSolfd project are (1) report on the effect on background AQ and transient PM peaks of using air purifiers; (2) refine our initial understanding of the AQ variations and sources generated by this first



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monitoring campaign by conducting a second campaign, doubling the amount of data available for source apportionment calculations.







### 1. INTRODUCTION

Inhalable air pollutant emissions from commercial vehicle fleets, from both the exhaust pipe and nonexhaust sources such as brakes and tyres, present a general health risk to the European population. Traditionally, studies and abatement of emissions of particles from road vehicles has focussed on exhaust emissions, although in recent years it has become clear that we should be equally concerned with non-exhaust pollution sources. This has been brought into sharp focus by the ongoing electrification of road transport which will gradually reduce exhaust emissions but not non-exhaust "wheel emission" particles released and resuspended from brakes, tyres, and road wear. In fact, such non-exhaust emissions are likely to increase in the future, due to the greater weight of battery-driven vehicles. For the immediate reduction of the scale of this air pollution challenge, retrofit solutions for tailpipe and brake emissions therefore need to be prioritised, brought to TRL 8, and introduced to the market by 2025. Timing is crucial: tailpipe retrofits are transition technologies until full electrification of Europe's transport fleet, but beyond this brake retrofits will continue to play an important role in the electrified fleet. Rapid gains in the reduction of the overall AQ footprint of existing public transport fleets are possible, using state-of-the-art retrofits for tailpipe, brake, and modern stationary air purifiers in semi-closed traffic-related micro-environments.

Within this context, the AeroSolfd project is especially focused on applying brake retrofit solutions directly close to the brake using a newly developed, easy adaptable and low-cost brake dust particle filter (BDPF) especially designed for long-lived public road transport vehicles such as buses and aimed at reducing 90% of the brake particle emissions. Using circular design approaches and retrofit solutions for semi-enclosed environments such as transport depots and underground stations, our proposed solutions are aimed to enhance existing air cleaning technology with an innovative stationary air purifier (FilterSquare), combined with smart solutions to reduce total concentrations of airborne particles. To better understand the present situation regarding air quality in these traffic-polluted microenvironments, we need to monitor background levels and use chemistry to consider likely pollution sources, particularly concerning the contribution of brake (and other non-exhaust) emissions to inhalable air pollutant particles: this is the challenge of deliverable 3.2.

### 1.1. PURPOSE AND TARGET GROUP

The primary purpose of D3.2 is to establish the background ("baseline") concentration levels of deeply inhalable (PM2.5) air pollutants inside the semi-enclosed, public transport-related microenvironment chosen for the AeroSolfd study. This essential database can then be compared to the conditions in which air purifiers are in use. Given the focus of the AeroSolfd project on reducing brake dust emissions, the baseline PM chemistry database needs to be interrogated to reveal the likely presence and chemical composition of metalliferous brake PM. While indoor rooms/halls are closed environments, the challenges of studying aerosol pollution within semi-enclosed vehicle hotspots such as bus depots and metro stations relate to the complexity of airflow in situations where public transport traffic is frequently moving in and out.





#### **1.2. CONTRIBUTIONS OF PARTNERS**

Table 1 Contribution of each partner in this deliverable

PARTNER SHORT NAME	CONTRIBUTIONS
CSIC	Lead the deliverable, carry out the AQ measuring campaign, chemically analyse the PM2.5 filters, write the report.
M+H	Provide support during the campaign and check deliverable
CARTIF	Development and installation of low-cost sensors and microprocessors. Support for the AQ measurement campaign in the AUVASA bus depot. Electrical installation for the different air purifiers setups.
AUVASA	Provide support during the campaign





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### 2. OBJECTIVES AND EXPECTED IMPACT

The overall goal is to develop a blueprint aimed at significantly reducing air pollution in public transport-related semi-enclosed micro-environments by using enhanced air purifier designs and innovative brake dust retrofit solutions.

### 2.1. OBJECTIVES OF D3.2

Task 3.2 has the following specific objectives:

1. Determination of the baseline (background) air pollutant levels present before the application of air purifiers and brake retrofit solution, as measured at specific locations representative of semi-enclosed public transportation pollution "hotspots".

2. Identify the presence of metalliferous air pollutants using chemical analysis of inhalable (PM2.5) aerosol particles sampled daily in the chosen test locations, review the likely anthropogenic aerosol inputs (e.g. from brake wear), and initiate an investigation aimed at quantitively revealing contributions of particles from different sources.

3. Initiate detailed field-testing of the impacts of innovative, eco-friendly air purifiers on air quality within a carefully chosen semi-enclosed public transportation centre, in this case, the semi-enclosed environment of the major bus depot of AUVASA in Valladolid, Spain.

#### 2.2. EXPECTED IMPACT

Understanding the background inhalable particle concentration levels and chemistry within the bus depot area is the first step on the road to improving air quality within this semi-enclosed public transportation micro-environment. Obtaining this database and defining background AQ, its chemistry, and likely PM sources, will allow us to determine the impact of both air purifiers and retrofit solutions on the air breathed by workers within the depot. The results of this and subsequent campaigns will be published in open access scientific journals, and communicated to the local companies and workers, following an increasing public awareness strategy focusing on 1) individual-level communication, and 2) empowering individuals and communities to advocate for policies that reduce air pollution.



### 3. DESCRIPTION OF TECHNICAL/SCIENTIFIC ACTIVITIES

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#### **3.1. DEMO SITE DESCRIPTION**

AUVASA bus depot is in Valladolid, a city in north-western Spain which has an area of c. 200 km<sup>2</sup>, an elevation of 698 m and a population of 302,000 (https://populationstat.com/spain/valladolid). The climate is subcontinental, with cold, foggy winters and hot, dry summers. AUVASA bus depot (Figs. 1 and 2) is situated 5 km south of the city centre, covers an area of 13,200 m<sup>2</sup>, and can accommodate up to 154 buses. Of these 154 total buses, at the time of the AeroSolfd campaign 28 were diesel, 46 LPG (liquid petroleum gases), 51 CNG (compressed natural gas), 18 hybrid and 11 electric (http://www.auvasa.es/auv\_opendata.asp). This fleet is controlled by 450 staff members who spend at least some of their working day active in the depot and therefore are potentially exposed to air pollutant emissions. During this air quality study, no exceptional construction or other engineering tasks took place, just regular vehicle maintenance work associated with oil changing, air filter cleaning, tyres, brakes, and sheet metal work involving sanding and use of fillers, primers and paints.



Figure 1 Plan of AUVASA bus depot and its surrounding environment



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Figure 2 Illustration of CSIC measuring equipment (grey machines front left) and M+H air purifiers (black & white square machines) at AUVASA bus depot. Note that the filtration is not part of this deliverable and will be published later.

#### **3.2. MONITORING EQUIPMENT**

This first AeroSolfd measurement campaign took place between 2023/05/16 and 2023/06/17, with baseline measurements (i.e. without using air purifiers) being made in the 1<sup>st</sup> week.

All equipment used and their location during the monitoring campaign are shown in Figure 3. PM2.5 concentrations were continuously monitored by means of a light-scattering laser photometer DustTrak (Model 8533, TSI), a desktop instrument able to provide real-time measurements of particulate matter on a 90° light scattering sensor over a wide concentration range  $(0.001 - 150 \text{ mg/m}^3)$  in real-time.

Particle number concentrations in the range  $10^3 - 10^6 \text{ #/cm}^3$  were monitored using a DiSCmini (Testo) that also records the size of the particles in a range of 10 - 300 nm (modal value) and 10 - 700 nm (absolute value). DiSCmini has high-time resolution of up to 1 second, but lower precision than a SMPS or CPC, with deviations of up to 30 %. It is sensitive to temperature and relative humidity, and the data can be erroneous at high temperatures. Particle number concentrations in the size range of 0.3 - 10 µm were obtained with an Optical Particle Sizer (OPS, Model 3330, TSI), a light, portable unit that provides fast and accurate measurement of particle concentration and particle size distribution using single particle counting technology in the size in up to 16 channels. Rigorous factory calibration standards ensure optimum measurement accuracy.

Black carbon (BC) concentrations were monitored using a microAeth<sup>®</sup> AE51 aethalometer, a pocketsized BC aerosol monitor which provides aerosol BC concentration in real-time in  $\mu g/m^3$ . It measures the rate of change in the absorption of transmitted light due to the continuous collection of aerosols deposited on a filter. The air sample is collected on T60 (Teflon-coated borosilicate glass fibre) filter media, with the data being recorded in an internal flash memory operating on a 30 second time resolution. The flow rate was set up to 0.10 L/min for measurements, with a measurement resolution of 0.001  $\mu g/m^3$  and precision of ±0.1  $\mu g/m^3$ .





ssenschaft Federal Department of Economic Education and Research EAER a State Secretariat for Education, Research and Innovation SERI In order to be able to identify the presence of brake wear particles using the chemical composition of PM2.5, a MCV high volume sampler was used. PM2.5 samples were collected using an automatic sequential high-volume sampler (HVS, Model CAV-A/MSb, MCV) equipped with an inlet (PM1025/UNE model, built according to the European Norm: EN 14907) with a specific nozzle plate for PM2.5. The sampler operates at a sampling flow rate of 30 m<sup>3</sup>/h. The airflow passes through the inlet and goes through the nozzles, where the speed increases. Then, the particles larger than 2.5  $\mu$ m in diameter impact and adhere on a plate impregnated with Vaseline and the smaller ones pass through and are collected on a quartz fibre filter (150 mm diameter; Pallflex).

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Figure 3 AQ monitoring equipment used (top) and choice of location (bottom). Locations where comparative 1hour measurements of median PM2.5 concentration ( $\mu$ g/m<sup>3</sup>) with CSIC equipment are illustrated by the 5 red circles. The chosen location for the equipment is marked by a yellow star, away from the main roadway but close to the workshop.





enschaft Federal Department of Economi Education and Research FARR State Secretariat for Education, Research and Innovation SERI In addition, a sensor box network was installed based on low-cost sensors (Sensirion SEN54 SDN-T, DFROBOT SEN0377), low-cost microcontroller (ESP32) and custom 3D printed housing (Figure 4). Sensirion SEN54 SDN-T is a sensor module that combines the measurement of different air quality parameters, namely particulate matter, VOC, humidity and temperature, while DFROBOT SEN0377 supports the detection of various gas concentrations, such as CO, C2H5OH (Alcohol), H2, NO2 and NH3.

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The sensor boxes send data to a developed data platform by means of wireless communication in the 2.4 - 2.5 GHz band (802.11b/g/n) and the use of the MQTT protocol. The data server platform allows real-time data monitoring, graphical visualisation, storage and data download of the sensor boxes.



Figure 4 Different assembly stages of the low-cost sensor boxes.

Twenty-one sensor boxes and 3 Wi-Fi routers were installed in the AUVASA bus depot (110 x 95 m) to analyse the PM level distribution over days and space. The sensors were distributed homogeneously along the whole area of the depot, as shown in Figures 5 and 6, and data have been collected since May 2023 until now.

The use of these customised sensor boxes allows to include other low-cost sensors, if necessary, at any of the demonstration sites. For example, it is also planned to use TERA (model NextST-URS) sensors in at least one of the monitored metro/train stations.



Figure 5 Layout of the installed and planned sensor boxes and routers in the AUVASA Bus Depot.



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Figure 6 Sensor boxes and Wi-Fi routers installed in the AUVASA Bus depot.

### **3.3. CHEMICAL COMPOSITION**

A total of 29 daily (24 h) filters from CSIC monitoring equipment were obtained during the May-June campaign. Before sampling, quartz microfibre filters were heated in an oven at 200°C during a minimum of 4 h to eliminate the volatile impurities. The filters were equilibrated for at least 48 h in a conditioned room (20°C and 50% relative humidity) and then weighed before and after sampling by means of a microbalance (Model XP105DR, Mettler Toledo). Filters were preserved individually in aluminium foils inside air sealed boxes and stored at room temperature under dry conditions until sampling or analyses, in case of blank and sampled filters, respectively. The gravimetric PM2.5 mass concentrations were determined by dividing the weight difference between the blank and sampled filter by the volume of air sampled. Final ambient concentrations were calculated after the subtraction of analytical blank values from the corresponding sample concentrations. Detection limits of the analysis techniques were calculated from the standard deviations from the blank filter analyses alongside the analytical uncertainties. The analytical procedures are the same used by Querol et al. (2012).

A filter section was acid digested using a mix of HF:HNO3 (5:2.5 mL) and then kept in a Teflon reactor at 90°C for at least 6 h. After cooling, the Teflon reactor was open and 2.5 mL of HClO4 were added. The acid solutions were then completely evaporated by placing the open reactors on a heating plate at 230 – 240°C. The dry residue was re-dissolved with 2.5 mL HNO3 to make up a volume of 50 mL with Milli-Q grade water, resulting a solution of 5% HNO3 This solution was then chemically analysed by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES: IRIS Advantage TJA Solutions, THERMO) and Mass Spectrometry (ICP-MS: X Series II, THERMO) to determine major (such as Al, Ca, K, Na, Mg, Fe, P, S) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Ba, La, Ce, Pr, Nd, Hf, W, Pb, Bi, Th, U, among others). For every batch of acid digested samples, corresponding blanks and field blanks were digested following the same analytical procedures. For quality control of the analytical procedure, a small amount (approx. 10 mg) of the Standard Reference Material 1633b (Coal Fly Ash) loaded on a similar fraction of a blank quartz microfibre filter was also analysed. The reference material analysis assures the quality of the results permitting the identification of possible analytical or calibration errors. Relative analytical errors were between 3 and 10% for the elements studied.



Organic (OC) and elemental carbon (EC) were determined by a thermal-optical transmission technique using a Sunset Laboratory OCEC Analyser with the NIOSH temperature program.

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### 4. RESULTS AND DISCUSSION

#### 4.1. SENSOR BOXES PM ANALYSIS

Data from the sensor boxes were analysed to assess the distribution of PM levels in the different areas of the AUVASA bus depot and to evaluate the variation of PM levels throughout the day. The conclusions of this analysis were taken into account for the definition of the location of the CSIC/NFA monitoring system and the location of the M+H air purifiers in T3.4. Data from the sensor boxes have been collected from May 2023. The sampling time was 1 minute, and the data averaged over 5 minutes were recorded in a database. The figure below shows the PM2.5 values ( $\mu g/m^3$ ) of one of the sensor boxes in the AUVASA bus depot throughout the day.



Figure 7 Sensor box #8 PM2.5 values in  $\mu g/m^3$  (2023/06/15).

The following figures show how the distribution of PM levels is quite homogeneous throughout the AUVASA depot and, as in the previous figure, how there are some specific periods of the day when PM levels are higher. Mainly in the early morning when most buses leave for their routes and at night when buses circulate inside the depot to take them to the washing and cleaning areas.



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Figure 8 PM2.5 values in  $\mu g/m^3$  from AUVASA bus depot sensor boxes (08 to16th June 2023).



Figure 9 Daily average of the cumulative PM X level in AUVASA bus depot (June 2023)

The data obtained with the laboratory equipment described in 3.2 are presented in the next sections.

### 4.2. PM2.5 AND BLACK CARBON MASS CONCENTRATIONS

An overview of the PM2.5 data is presented in Figures 10 and 11 and Table 2. The 24 h mass concentration of ambient PM2.5 recorded by the gravimetric filter samples measured at the AUVASA sites during the first week show a background (baseline) average of  $27.1 \,\mu\text{g/m}^3$ , whereas for the entire 29-day AQ monitoring campaign the average was 24.7  $\mu$ g/m<sup>3</sup>. Daily (24h) averages ranged between a minimum of 16.7  $\mu$ g/m<sup>3</sup> (on 27th May) and a maximum of 39.8  $\mu$ g/m<sup>3</sup> (on 18th May). Similar PM2.5 mass concentrations overall were recorded by the DustTrak equipment, which measures every 5 minutes (Table 2). These PM2.5 concentration levels were consistently above those measured at the nearest official outdoor AQ monitoring station within Valladolid (i.e. the Vega Sicilia roadside AQ monitoring site, which lies ~ 900 m WNW of the AUVASA building). Similar concentrations were observed at several bus stations (Wang et al., 2011; Cheng, Chang and Yan, 2012; Lee et al., 2017). The boxplots on Figure 10 demonstrate this difference by comparing hourly PM2.5 concentrations (both averages and ranges) inside the bus depot with those measured at Vega Sicilia. Average levels of PM2.5 at Vega Sicilia were 6.3  $\mu$ g/m<sup>3</sup>, which is much lower than the average mass concentrations measured in the bus depot (26.8  $\mu$ g/m<sup>3</sup>), with no overlap between the two interquartile ranges (shown in red and blue on Figure 10. Note also the presence of a morning "rush-hour" peak after 07.00 when normal daytime commuting activity begins, and the fact that morning periods are generally more polluted than those in the afternoon (Figure 10).





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*Figure 10 Daily distribution of baseline (BL) PM2.5 at AUVASA bus depot and outdoor (Vega Sicilia air quality official monitoring station) environment. The dots represent the average.* 

Table 2 Summary statistics for PM2.5 concentrations registered with a DustTrack equipment every 5 minutes during the whole campaign.

<u>ΡΜ2.5 (μg/m³)</u>			
AUVAS	A	Outdoor (Vega Sicilia)	
Range (Min-Max)	11.3 – 136.9	Range (Min-Max)	1.0-18.0
Mean	26.8	Mean	6.3
Median	25.1	Median	6.0
St. Dev	9.5	St. Dev	3.7
Count	8491	Count	718

Examining the data on a more detailed timescale reveals PM2.5 concentrations to record sharp, transient peaks within each 24-hour period, as demonstrated by Figure11 which shows a time series of PM2.5 and BC levels throughout one day. The exact timing of the peaks varies from day to day, with the exception of the 07.00 initial rush hour peak, which is a regularly repeated daily event. Another observation is that peaks in air pollutants are common during the early morning. The example provided by Figure 11 shows enhanced levels of PM2.5 after 01.00, with a prominent peak after 04.00. Such peaks are interpreted as recording PM emissions during night works within the bus depot.



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*Figure 11 Time series of PM2.5 and BC during 2023/06/01, illustrating the presence of transient air pollution peaks (see text for discussion).* 

The frequent occurrence of transient air pollution peaks within the bus depot air is well demonstrated in Figure 12, which shows variations in PM2.5 mass concentrations throughout the entire monitoring period. These transient peaks can on occasion exceed PM2.5 concentrations of 100  $\mu$ g/m<sup>3</sup> (Figure 12).



Figure 12 Time series of PM2.5 at AUVASA bus depot for the whole campaign.

BC measurements also reveal extreme short-term variation in air quality, presumably primarily linked both to the movement of buses through the depot during the day, and to exhaust emissions during maintenance works. The regular repetition of the morning rush hour event is also an obvious characteristic of the BC data, with levels typically rising suddenly soon after 07.00. In several cases BC concentrations levels exceeded 5  $\mu$ g/m<sup>3</sup> and stayed high for 30 min or longer during this rush period. An exceptional case is provided on 14th June when the morning rush hour peaked at 07.15 with BC values of 27.8  $\mu$ g/m<sup>3</sup>.





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Average daily variations in number concentrations of inhalable particles of three different size fractions are shown in Figure 13. Once again, the presence of the 07-08.00 morning rush hour when the daily schedule begins is clear, especially in the finest particle sizes (0.3-1  $\mu$ m). The sources of these fine particles likely include both fuel combustion emissions and brake wear: Sanders et al. (2003), for example, has demonstrated that number concentrations of brake pad wear particles typically peak in the size range 0.5-1.5  $\mu$ m. The contrast between the abundant presence of these finer particles in the morning ambient air as compared to the afternoon is also well demonstrated. Also discernible in Figure 13 is the early morning (04-05.00) activity attributed to vehicle maintenance work.

#### 4.3. PM2.5 CHEMICAL COMPOSITION

The chemical analyses for the 29 filter samples collected during the May-June 2023 campaign at AUVASA bus depot are summarised in Figure 14. The two dominant chemical components present in the PM2.5 analyses are organic carbon (OC): and rock-forming mineral dust ("Mineral" in Figure 14: note ammonium salts are not analysed). Organic carbon particles comprise a complex mixture of carbonaceous materials that include primary and secondary natural and anthropogenic volatile and semi-volatile organic compounds, bioaerosols such as pollen and microbes, and organic soil particle resuspension. A proportion of the anthropogenic organic carbon particles present in ambient city air derives directly from brake wear (Gasser et al., 2009). In contrast, mineral particles are mostly silicates





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and carbonates of geological origin from rocks and soils, such as quartz, clay minerals, and calcite. In the Valladolid data these two components OC and Mineral are typically present in similar concentrations ( $4.5 \mu g/m^3$ ), and they show a generally good correlation with total PM2.5 mass (Figure 15), indicating they are the main contributors to PM mass concentrations.

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Figure 14 Chemical composition of all samples collected in AUVASA bus depot, separating average value for all samples (AVE), average for the first week without air purifiers on (AVE BL 1st week), average all other days when air purifiers were not operating (AVE BL other days) and average for all days when air purifiers were on (AVE AP).



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Figure 15 Comparison between mass concentrations of organic carbon (OC), rock-forming mineral dust (Mineral), and total PM2.5. In most cases, peaks define similar broad patterns, although there are some exceptions, such as the prominent mineral dust peak on 6th June.

Elemental carbon (EC), typically produced by the incomplete burning of carbonaceous matter and a marker for traffic emissions such as diesel exhaust, is present in much lower quantities than OC (OC/EC average 4.5) within the Valladolid dataset and does not correlate closely with any other chemical component.

#### Metalliferous Pollution Peaks

With regard to metal content, the average Fe content of the AUVASA PM2.5 samples is 0.7  $\mu$ g/m<sup>3</sup>, although daily values range across an order of magnitude (0.2-2.5  $\mu$ g/m<sup>3</sup>). Peaks in Fe content are typically associated with enhanced levels of several trace metals, which is of particular interest because such metals can reveal valuable data regarding anthropogenic particle sources. In the context of the AeroSolfd project, it is the trace metals that are most likely to be useful when investigating the content of brake emissions in ambient aerosols.

During the first week of sampling, when air purifiers were not in use, the commonest trace metals present in the PM2.5 filters are Zn (average 30 ng/m<sup>3</sup>, range 17-46 ng/m<sup>3</sup>), followed by Cu (average 24 ng/m<sup>3</sup>, range 6-75 ng/m<sup>3</sup>), Ba (average 24 ng/m<sup>3</sup>, range 10-50 ng/m<sup>3</sup>), Ti (average 21 ng/m<sup>3</sup>, range 11-25 ng/m<sup>3</sup>), and Sb (average 13 ng/m<sup>3</sup>, range 3-44 ng/m<sup>3</sup>). The same 5 elements dominate the trace metal averages for the entire sampling period, although with some changes in the order, from Zn>Cu>Ba>Ti>Sb to Zn>Ba>Ti>Cu>Sb: Zn (average 44 ng/m<sup>3</sup>, range 12-241 ng/m<sup>3</sup>), Ba (average 28 ng/m<sup>3</sup>, range 7-56 ng/m<sup>3</sup>), Ti (average 24 ng/m<sup>3</sup>, range 11-86 ng/m<sup>3</sup>), Cu (average 18 ng/m<sup>3</sup>, range 4-75 ng/m<sup>3</sup>) and Sb (average 11 ng/m<sup>3</sup>, range 3-44 ng/m<sup>3</sup>). These 5 metals/metalloids together comprise 80% of the trace element content measured in the filter samples. The 5 next most common trace elements present are Mn>Pb>Cr>Sr>Zr>Sn, with average values descending from 7 to 2 ng/m<sup>3</sup>.

Figure 16 compares the Fe and trace metal content of the AUVASA samples with those of a previous air sampling PM2.5 study undertaken while walking outside through the busy streets of Barcelona



(Moreno et al., 2015), as an example of urban air. This comparison reveals how the AUVASA samples are strikingly poorer in Zn, probably sourcing from tyre wear abundantly present in the traffic-polluted city street air. Iron and Ti will likely derive from mixed sources but especially "crustal" mineral dust contaminating the city streets from construction sites and vehicle resuspension. Regarding elements more typically attributed to brake wear, Cu shows much less difference, Ba is similar in all samples, and Sb is notably higher in the AUVASA data, together suggesting a higher relative amount of brake dust present in the bus depot.

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Figure 16 Average concentrations of 9 metals measured in background ambient air within the AUVASA depot during the first week of the AQ monitoring campaign (green) as compared to averages for the entire campaign (orange) and published results in the traffic-polluted streets of Barcelona city centre (Moreno et al., 2015) (blue).

The wide range of concentrations recorded by metals such as Fe (0.2-2.5  $\mu$ g/m<sup>3</sup>), Cu (6-75 ng/m<sup>3</sup>) and Sb (3-44 ng/m<sup>3</sup>) is due to the presence of "metalliferous peaks" on five of the sampling days, namely the 22nd and 29th May, and the 1st, 6th, and 12th June, as shown on Figure 17. Each of these metalliferous pollution events is considered below in more detail.

Monday 22nd May. This event is characterised by unusually elevated levels of **Fe (2.5 \mug/m<sup>3</sup>), Cu (75 ng/m<sup>3</sup>), Ba (50 ng/m<sup>3</sup>), and Sb (44 ng/m<sup>3</sup>).** In addition, although all present at much lower concentrations, Cr (11 ng/m<sup>3</sup>), Sn (6 ng/m<sup>3</sup>), Ni (3 ng/m<sup>3</sup>), Bi (1.2 ng/m<sup>3</sup>), V (1 ng/m<sup>3</sup>), Co (0.5 ng/m<sup>3</sup>) and W (0.2 ng/m<sup>3</sup>) on that same day all attain their maximum levels recorded during the sampling campaign (Figures 14 and 17). Levels of S (1  $\mu$ g/m<sup>3</sup>), Mn (19 ng/m<sup>3</sup>) and As (0.6 ng/m<sup>3</sup>), and mass concentration of PM2.5 (31  $\mu$ g/m<sup>3</sup>) are all also notably higher than average. On this day, PM2.5 concentrations were unusually high for the first 12 hours (average 45  $\mu$ g/m<sup>3</sup>) with an exceptional pollution peak recorded between 04.05-04.15 am in the early morning, when PM2.5 levels exceeded 100  $\mu$ g/m<sup>3</sup>, peaking at a 5-minute average of 148  $\mu$ g/m<sup>3</sup>. The same event was recorded by BC data which rose suddenly to an exceptional peak of 23.7 ng/m<sup>3</sup> at 04.15. It is considered likely that this event, probably related to night maintenance work, was responsible for the unusually high average levels of metals recorded that day.



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Figure 17 Multi-element time series plot showing variations in the daily average concentrations of 9 metals present within ambient air of the AUVASA bus depot throughout the monitoring campaign. Five peaks are evident, defined most clearly by Fe and Zn concentrations. See text for details.

Monday 29th May. This event is characterised by unusually elevated levels of **Ti** (86 ng/m<sup>3</sup>), accompanied by Mo (9 ng/m<sup>3</sup>), Zr (7 ng/m<sup>3</sup>) and a range of rare trace elements such as Sc, Y, HREE, Th, Hf and Ge all registering their highest concentrations measured in the sampling campaign (all <1 ng/m<sup>3</sup>: Figure 14). Levels of Ba, Sr, Sb, Al2O3, and mass concentration of PM2.5 (31  $\mu$ g/m<sup>3</sup>) are also notably higher than average. Note also that these data record the lowest Cu/Fe ratio of the campaign (0.016). Unlike the exceptionally metallic event recorded on the previous Monday (22nd) the data do not record unusually elevated pollution levels throughout that day, apart from a brief (5 minute) PM2.5 peak of 79  $\mu$ g/m<sup>3</sup> timed at 21.07 am, and a BC transient peak of 12  $\mu$ g/m<sup>3</sup> at 10.55 am.

Thursday 1st June. This event is characterised by unusually elevated levels of Zn (147 ng/m<sup>3</sup>) and Pb (14 ng/m<sup>3</sup>), concentrations of Ca (1  $\mu$ g/m<sup>3</sup>), Sb (21 ng/m<sup>3</sup>) and Sr (4 ng/m<sup>3</sup>), Sn (3 ng/m<sup>3</sup>) all also notably higher than average. Concentrations of PM2.5 averaged 27  $\mu$ g/m<sup>3</sup> that day and were at their highest early in the morning (averaging 41  $\mu$ g/m<sup>3</sup> from 00.30-04.30, with a peak of 59  $\mu$ g/m<sup>3</sup> at 04.20 am). Similarly, levels of BC averaged 1.8  $\mu$ g/m<sup>3</sup> for the 24h period but this figure over doubled during the early morning (average of 3.9  $\mu$ g/m<sup>3</sup> for 0.30-05.00, with a peak of 13.9  $\mu$ g/m<sup>3</sup> at 04.30). As with the pollution event on Monday 22nd May, air quality, as measured by PM2.5 and BC, was at its worst during the early morning, before the main bus fleet was operative.

Tuesday 6 June. This event is characterised by the highest levels of **mineral dust (13 \mug/m<sup>3</sup>)**, with corresponding concentration maxima recorded by **Al2O3 (1.8 \mug/m<sup>3</sup>)**, **Ca (1.4 \mug/m<sup>3</sup>)**, **Mg (0.21 \mug/m<sup>3</sup>)**, **P (65 ng/m<sup>3</sup>)**, **Ba (65 ng/m<sup>3</sup>)**, **Mn (36 ng/m<sup>3</sup>)**, and **Sr (6 ng/m<sup>3</sup>)** as well as Li, As and Ga (all <1 ng/m<sup>3</sup>). Levels of Fe (1.6  $\mu$ g/m<sup>3</sup>), Cu (46 ng/m<sup>3</sup>), Ti (44 ng/m<sup>3</sup>), Sb (26 ng/m<sup>3</sup>), Cr (9 ng/m<sup>3</sup>), Pb (8 ng/m<sup>3</sup>), Sn and La (both 4 ng/m<sup>3</sup>), Ce (3 ng/m<sup>3</sup>), Ni (2 ng/m<sup>3</sup>), Rb, Co, Ge, Cs, Nd, W and mass concentration of PM2.5 (35  $\mu$ g/m<sup>3</sup>) are all also notably higher than average. Neither PM2.5 nor BC data record unusual pollution events that day, with only brief increases in levels soon after 04.00 and 07.00. Outdoor



conditions that day were cleaner than usual (24 h average of only 3  $\mu$ g/m<sup>3</sup> at Vega Sicilia, as compared with an average of 6  $\mu$ g/m<sup>3</sup> for the monitoring campaign), so the PM source appears to have been generated inside the depot.

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Monday 12th June. This event is characterised by unusually elevated levels of **Zn (241 ng/m<sup>3</sup>).** Unlike during the Zn-rich pollution event recorded on 1st June, in this case Mn concentrations were notably above average whereas Pb levels and PM2.5 were both below average. Thus, these two events, although both involving Zn emissions, do not appear to be chemically similar. Neither PM2.5 nor BC data record unusual pollution events that day.

In addition to the five events listed above, Thursday 8th June registered unusually high levels of the light rare earth elements La and Ce, with an unusually elevated La/Ce ratio (1.6) indicating a pollution source relatively rich in La. Another exceptional trace element peak was the maximum concentration of Se (along with high Mo) recorded on Sunday 4th June, and EC showed a maximum value on Wednesday 14th June. Finally, at the start of the campaign the notable presence of secondary organic compounds is suggested by elevated levels of OC, S, V, K, Na, and PM2.5 mass concentrations, this trend appearing to repeat itself at the end of the campaign. It is clear from overviewing the chemical data that different sources are contributing to the PM2.5 trace element content within the AUVASA depot.

#### Investigating the contribution of brake emissions

The complexity of brake dust chemistry stems from the many different functional components used as fillers (e.g. calcite, barite, silicates, rubber, chromium oxide, antimony sulphate), binders (e.g. phenolic resins), fibres (e.g. metals, carbon, glass, Kevlar polymer), lubricants (e.g. graphite, metal oxides and sulphides like Sb2S3), and abrasives (e.g. oxides of Fe, Al, Si, Zr) (Thorpe and Harrison, 2008; Grigoratos and Martini, 2015; Kukutschová and Filip, 2018; Harrison et al., 2021). In addition to the presence of OC, therefore, brake emission particles are typically highly metalliferous, with Fe and Cu being dominant (Hulskotte et al., 2014). Copper, in particular, is widely used as a tracer for brake dust, and it has been calculated that brakes release over 50% of European atmospheric Cu emissions (Denier Van der Gon et al., 2007). Other metals reported as being present in brake emissions include Sb, Sn, Zn, Pb, K, Ti, Ba, Mn, Mg, Ni, Cd, Cr, Zr, and Mo, depending on the chemistry of the brake pads being investigated (Garg et al., 2000; Westerlund and Johansson, 2002; Sanders et al., 2003; Chan and Stachowiak 2004; lijima et al., 2007, 2008; Thorpe and Harrison, 2008; Gasser et al., 2009; Kukutschová et al., 2009, 2011; Figi et al., 2010; Gietl et al., 2010; Apeagyei et al., 2011; Amato et al., 2012; Harrison et al., 2012; Kam et al., 2012; Pant and Harrison, 2013; Peikertová et al., 2013; Grigoratos and Martini 2015; Hagino et al., 2016; Charron et al., 2019; Güney and Öz, 2020; Harrison et al., 2021; Fussell et al., 2022; Lopez et al., 2023; Švábenská et al., 2023).

Of the metals present in brake dust, just four, namely Fe, Cu, Zn and Sn, comprised 80-90% of metals in 65 car brake pads analysed by Hulskotte et al. (2014), and Fe comprised around 95% of brake discs. Note however that different brakes can vary greatly in their chemical compositions (especially in, for example, their Zn content), and over 3000 types of material have been reported from different brands of brake linings (Roubicek et al., 2008). In the case of the AUVASA bus depot study, the following brake



senschaft Federal Department of Economic Aff Education and Research EAER State Secretariat for Education, Research and Innovation SERI brands were in use (vehicle in brackets): JURID REF 2913109560 (IVECO URBANWAY), JURID REF. 2925305390 (MAN A21-A24 // MB-CITARO // VECTIA), JURID REF. 2903009560 (MAN J22), OPTILINE REF. OPTI-030-400 (SOLARIS URBINO 12/18). We do not have direct information on the chemical compositions of these brakes.

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According to a list of 29 publications compiled by Grigoratos and Martini (2015) and Harrison et al. (2021), the two trace metals most commonly used in the calculation of brake wear emission factors, are Cu and Sb, with Fe, Ba, Pb, Zn, Zr, Cd, Ni and Sn also having been utilised but to a lesser degree. Emission factors for Cu, Fe, Sb and Sn are much higher (around an order of magnitude) for heavy vehicles than for cars (Charron et al., 2019). Publications focussing on the emission of such metalliferous brake-derived particles have estimated that up to 70% can become airborne but there is wide variation in the data (Hagino et al., 2016; Harrison et al., 2012; Straffelini et al., 2015; Perricone et al., 2017).

Another approach to characterising the chemistry of brake dusts is to use metal ratios such as Cu/Fe and Cu/Sn. Charron et al. (2019) for example suggested that Cu/Fe ratios of 0.04 were typical of brake dust from European cars. Using a similar approach, various authors have examined Cu/Sb ratios measured in brake dust, although there is again wide variation in results from different studies, with reported Cu/Sb varying from 1-12 (Sternbeck et al., 2002; Pant and Harrison 2013; Charron et al., 2019), probably due to differences in brake pad composition, vehicle types and particle sizes analysed (PM10 v PM2.5).

In this context, with regard to metal ratios in the AUSAVA PM2.5 data, these show Cu/Fe values averaging 0.026 (range 0.016-0.031), Cu/Sb averaging 1.65 (0.77-2.35), Cu/Sn averaging 9.4 (3.3-16.8), and Cu/Ba 0.63 (0.21-1.50). These results are generally comparable to metal ratios in traffic-contaminated dust published elsewhere, although one notable exception is Sb, which is enriched in the AUVASA filter samples. For example, comparing our data in the bus depot with metal ratios recorded from roadside exposure to traffic-contaminated dust in central Barcelona, whereas the Cu/Fe ratios in both case are 0.03, the Cu/Sb ratios are 18 for the Barcelona outdoor roadside data but only 1.65 in AUVASA (Moreno et al., 2015). Interestingly, however, Sb levels recorded inside the bus depot (11 ng/m<sup>3</sup>) lie within the range of Sb concentrations reported from inside Barcelona buses (11-25 ng/m<sup>3</sup>: Moreno et al., 2015). One explanation for this would be that notable amounts of Sb are present within the brakes used by both Valladolid and Barcelona (and probably other city) buses.

Statistical examination applying Pearson methodology to the 29-sample group of the AUVASA PM2.5 filters reveals extreme positive coefficients of correlation (r > .91) between the following metal pairs: Fe-Cu (r = .99), Cu-Sb (r = .97), Fe-Sb and Cr-Sn (r = .96), Fe-Sn (r = .95), Fe-Cr and Cu-Sn (r = .92). Figure 18 demonstrates these correlations, illustrating the likelihood of a common source for these five metals, namely Fe, Cu, Sb, Sn, and Cr. Given the published literature on brake chemistry outlined above, therefore, we suggest that concentrations of these five metals present in the AUVASA samples are derived largely from brake emissions. In the case of Ba, also commonly used as a tracer for brakes, correlation coefficients are less robust but still positive (Ba-Cu r = .66; Ba-Fe r = .66; Ba-Sn r = .59; Ba-Cr r = .71; Ba-Sb r = .68), suggesting additional sources other than brakes for this element. In notable contrast, concentrations of Zn show no affinity with our five identified "brake metals" (Zn-Cu r = .16, Zn-Fe r = .17, Zn-Cr r = .18, Zn-Sb r = .2). This leads us to suggest that Zn in our database



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senschaft Federal Department of Economic A1 Education and Research EAER State Secretariat for Education, Research and Innovation SERI is likely to be sourced primarily from tyre and not from brake wear, reinforcing the fact that in published research literature Zn is the metal most commonly used as a tracer for tyre wear (e.g. Harrison et al., 2021). We predict from these observations that Zn is not a major component of the brakes used by the buses stationed in the AUVASA depot.

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Another approach is to use receptor models to interpret PM time series data and identify likely sources of unusual concentrations and to apportion their contributions to total mass. Even in cases where information on source emissions is not available, the application of multivariate factor analysis using, for example, positive matrix factorisation (PMF) can reveal and apportion likely pollution sources. An early example is provided by Bukowiecki et al. (2010) who calculated PM10 traffic emissions in a Swiss street canyon to comprise 21% brake wear, 38% resuspended road dust and 41% exhaust emissions respectively, with the contribution from brakes falling to just 3% on the open highway. In many cases, however, such studies have failed to isolate the specific contribution from brake dust to traffic emissions (e.g. Pant and Harrison, 2013; Crilley et al., 2017; Liu et al., 2023), and the majority of these publications report on PM10, not PM2.5. In a recent study by Scerri et al. (2023) PMF calculations on roadside PM10 revealed the presence of "crustal" (mineral) dust and "brake-tyre" particles (with the latter comprising 17% of total mass), but could not differentiate between brakes and tyres. In contrast, another recent publication (Beddows et al., 2023), did manage to successfully isolate a PM10 brake component at a roadside/construction site in Birmingham, UK, calculating 83% crustal mineral dust, 9.6% tyre dust, and 7.1% brake dust.









Figure 18 Correlations between brake-dust generated metals such as Fe, Cu, Sb, Sn and Cr are strongly positive, although Ba is less well correlated, probably due to mixed sources. Zinc does not correlate with "brake dust" metals in the AUVASA data and probably is derived mainly from tyre wear (see text for details).

In order to apply source apportionment tools involving receptor models, however, a sufficiently large number of analyses is necessary. The minimum number of samples required for a study using PMF for example can vary depending on several factors, including the complexity of the system, the variability of the sources, and the statistical significance desired in the results. To ensure the reliability and robustness of a PMF analysis of the AUVASA data, we consider a minimum of 50 filter sample analysis is necessary. Given that the May-June 2023 monitoring campaign yielded a total of only 29 samples for chemical analysis, we plan to double the sample number by adding filters to be obtained in a repeat campaign at AUVASA during 2024, to obtain a robust PMF-driven source apportionment result.





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### 5. DEVIATIONS FROM THE PLAN

Due to unexpected delays in beginning the monitoring campaign in the Metro of Lisbon, related mainly to unexpected difficulties encountered regarding the equipment delivery and instalment, only results from the first measurement campaign (in Valladolid) can be shown in this deliverable. A PMF numerical estimation of the brake source contribution is planned once the second measuring campaign in AUVASA bus depot has been completed (it will follow the Metro study in Lisbon).

### 6. LINKS WITH OTHER WPS

Due to the delay in the timing for the monitoring campaign in Lisbon it is possible that there will be knock-on effects for deliverables such as D3.3 and D.3.4, although we are working to minimise this. No other WPs should be affected.

WP3 is closely related to WP4 (Sustainability Assessment) and WP5 (Dissemination and Exploitation), as the data generated will be used in all of them.







### 7. CONCLUSIONS AND RECOMMENDATIONS

Our results from the AUVASA bus depot study demonstrate that:

(1) Daily AQ inside the bus depot is generally better than in many transport-polluted urban microenvironments but is highly variable due to the presence of frequent transient peaks in air pollutants. For comparison, average background concentrations of  $27 \ \mu g/m^3$  inside the AUVASA depot are lower than those measured inside buses, subway trains and even (in most cases) outdoor street walking in Barcelona (Moreno et al., 2015).

(2) Daily AQ as measured by inhalable particle mass is usually worse at the start of the working day soon after 07.00, when a "rush hour" peak is common, and can be lower than average during the night/early morning, probably due to emissions released during maintenance work.

(3) Transient peaks in the concentrations of metalliferous particles in some cases appear to be associated with early morning maintenance work before the morning rush hour.

(4) The presence of inhalable particles released from brakes is strongly suggested by transient concentration peaks and extremely close correlations between classic "brake-related" elements, notably Fe, Cu, Sb, Cr and, to a lesser extent, Ba.

(5) The presence of particles released from tyres is suggested by transient peaks in the concentration of Zn, this metal being derived from a source other than the "brake related" elements.

(6) Improvements in ventilation and/or use of air purifiers, especially during rush hour peaks and when maintenance work is being performed, are the most obvious ways to improve AQ and the quality of the working environment for the employees working in the depot.

(7) Doubling the size of the existing PM chemistry database will make possible a more robust numerical estimation of non-exhaust emissions present within the AUVASA depot, using PMF multivariate factor analysis.





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