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VALIDATION OF ROADSIDE VEHICLE EMISSION SENSING BY TAILPIPE TESTS

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Remote sensing of motor vehicle emissions for the purpose of identifying high emitting vehicles is a complementary measure to the periodic technical inspection tailpipe tests. The focus of this thesis is an experimental validation of roadside measurement of particulate matter emissions of individual vehicles. The validation is to be conducted by passage of vehicles with known emissions characteristics through roadside measurement point and/or by tailpipe tests of selected vehicles. As a minimum requirement, the ability to discern between vehicles with and without a functional diesel particle filter is to be established, with any additional insights, such as differentiating between spark ignition and compression ignition engines or identification of non-stoichiometric air-fuel ratio or defunct three-way catalytic converter on spark ignition engines, highly welcome. The work requires active participation at tests conducted by the Czech University of Life Sciences within the City Air Remote Emissions Sensing (CARES) project.

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(1) Bishop, G. A., et al. (1989). Environmental science & technology, 49(3), 1639-1645. // (2) Bishop, G. A., et al. (2015). Environmental science & technology 49.3 (2015): 1639-1645. // (3) Bischof, O. (2015). Emiss. Control Sci. Technol., 1, 203-212. // (4) Hallquist, A. M., et al. (2013). Atmospheric Chemistry and Physics, 13(10), 5337-5350. // (5) Preble, C.V., et al., Environ. Sci. Technol. 2015, 49, 8864–8871

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I hereby declare that the following thesis is my independent work and to the best of my knowledge. I duly marked out all quotations. All information used from literature and sources has been acknowledged in the text with the list of references.

Koushik Vijayakumar

Place: Prague Date: 11th August 2023

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List of Abbreviations

ANPR	Automated Number Plate Recognition
СО	Carbon Monoxide
CO ₂	Carbon Dioxide
CTU	Czech Technical University
CZU	Czech University of Life Sciences
DPF	Diesel Particulate Filter
EEA	European Environment Agency
EEPS	Engine Exhaust Particle Sizer
EF	Emission Factor
EGR	Exhaust Gas Recirculation
EU	European Union
FTIR	Fourier Transform Infrared Spectrum
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
IR	Infrared Ray
LCV	Light-Commercial Vehicle
LNT	Lean NOX Trap
LOD	Limit of Detection
LOQ	Limit of Quantification
LPG	Liquified Petroleum Gas
LTC	Low Temperature Combustion
Ν	Nitrogen
NA	Not Available
NH ₃	Ammonia

NO	Nitric Oxide
NO ₂	Nitrogen Dioxide
NO _X	Nitrogen Oxides
nvPN	Nonvolatile Particle Number
O ₂	Oxygen
OH	Hydrogen Oxide
PCCI	Premixed Charged Compression Ignition
PEMS	Portable Emissions Measurement System
PM	Particulate Mass
PM ₁₀	Particulate Matter with diameter >10 µm
PM _{2.5}	Particulate Matter with diameter >2.5 µm
PN	Particulate Number
PTI	Periodic Technical Inspection
R2	Correlating Factor
RCCI	Reaction Controlled Compression Ignition
SCR	Selective Catalytic Reduction
UHC	Unburnt Hydrocarbon
WHO	World Health Organization

1. Abstract

Remote sensing of motor vehicle emissions for the purpose of identifying high emitting vehicles is a complementary measure to the periodic technical inspection tailpipe tests. The focus of this thesis is an experimental validation of roadside measurement of particulate matter emissions of individual vehicles by remote sensing method in the real driving world. The validation of the roadside measurement is conducted by passage of vehicles with known emissions characteristics through roadside measurement point with the tailpipe measurement of selected vehicles, by which the measurement is recorded and analyzed by linear regression method for concentration of Pollutants with respect to concentration of carbon dioxide, considering the applicable factors to obtain Emission Factors of each individual vehicles. The obtained Emission Factors is compared with data of tail measurements for correlation to give the information regarding the ability to discern between vehicles with and without a functional diesel particle filter and to categorize and determining Low emitters and High Emitters. The experiment resulted in good correlation of PN emission factors with the tail pipe measurements giving additional insights regarding the two different modes of measurement methods and the instruments for used for remote emission sensing and their suitability.

Keywords: Remote Emission Sensing (RES), Nitrogen Oxides (NO_X), Particulate Matter,
Particulate Number (PN), Emission Factor (EF), High Emitter, Low Emitter,
Sampling point, Engine Exhaust Particle Sizer (EEPS), Nanomet3 (NM3),
linear Regression

2. Introduction

The Majority of Air Pollution is by Road traffic. Road traffic emits both gaseous and particulate pollutants and is a substantial source of Nitrogen oxides and particulate matter emissions. The presence of these hazardous pollutants in the atmosphere deteriorates Air quality, Human health and impacts Climate and the Ecosystem. Many of the Road transport vehicles in Europe emit Emissions at rates higher than the corresponding nominal legislative limits when driven in actual driving scenarios which is a major problem in metropolitan regions, which could affect the population and the vegetation and are responsible for thousands of premature deaths each year. The problems with urban air quality in European cities have worsened by this excess emissions source being defective or tampered exhaust treatment technologies. Due to the nature of the damage and EU emission standard rules, it is required to distinguish and assess the vehicles which emit high emissions and provide suggestions for prospective repairs for their Exhaust after treatment devices or removal from the transportation fleet, which is an effective technique for improving air quality. EU emission standard rules for exhaust emissions have set emission limitations with the introduction of modern technology solutions, both for vehicles of all categories from light weight passenger cars to heavy weight trucks and buses to enhance air quality and to reduce pollutant concentrations in air.

The European Emission Regulatory Board has introduced a method of more representative laboratory emission testing which is Real – Driving Emissions (RDE) tests using Portable emissions measuring systems (PEMS) and Remote sensing of exhaust emissions. PEMS and remote sensing were developed to determine true emissions. One of the most frequent ways for measuring emissions in a controlled setting is PEMS, a time-consuming method and an expensive method that is used to monitor vehicle emissions in a range of conditions. Remote sensing is the most efficient measuring approach since it allows for the measurement of many cars in a short period. In this experiment, a remote sensing measuring approach and tail pipe measurement were both used to measure vehicles emissions, analyze the test and to validate the results from both type of measuring methods from the vehicles fleet and to identify the high emitters from the fleet of vehicles tested.

2.1 Vehicle emissions.

Vehicle emissions can be mainly categorized into 3 ways, and they are as follows.

1.<u>Exhaust Emissions</u> - Emissions created by the burning of petroleum fuels such as gasoline, diesel, natural gas, and LPG, which are hydrocarbon mixtures. There is no such thing as a flawless engine that creates no pollution. This thesis is entirely focused on exhaust emissions.

2. <u>Abrasion Emissions</u> - Emissions created by mechanical abrasion and corrosion of vehicle parts. It oversees particulate matter emissions. Mechanical abrasion of tires, brakes, and clutches, road surface wear, and corrosion of chassis and other vehicle components all contribute to this issue.

3.<u>Evaporative Emissions</u> - Emissions created by the evaporation of vapors from the vehicle's fuel. This occurs when VOCs are used. When the vehicle is stopped with the engine switched off or operating with the engine turned on, petrol fuel vapors containing various hydrocarbons attempt to escape from the gasoline in the tank. This Thesis is concentrated on the Evaporative emissions.[1]



2.2 Major Pollutants on Road and their impacts

Figure 1 Impact of emission process cycle [1]

1.Hydrocarbons (HC) Hydrocarbons (HC) are a type of volatile organic compound that are emitted by vehicles. They are composed of hydrogen and carbon atoms and are released into the atmosphere because of incomplete combustion of fuel in the engine. HC emissions can come from a variety of sources, including fuel evaporation, engine oil, and incomplete combustion of gasoline. HC emissions from vehicles have negative impacts on both human health and the environment. They contribute to the formation of ground-level ozone, which can cause respiratory problems and aggravate asthma.

HC emissions also contribute to the formation of smog, which can lead to decreased visibility, acid rain, and damage to crops and ecosystems. To reduce HC emissions from vehicles, many countries have established emissions standards for new vehicles. These standards require that vehicles meet certain limits on HC emissions, which can be achieved using technologies such as catalytic converters, improved fuel injection systems, and improved engine design. Regular vehicle maintenance, such as oil changes and tune-ups, can also help reduce HC emissions from older vehicles.

2.Carbon Monoxide (CO) - Carbon monoxide (CO) is a colorless, odorless gas that is emitted from vehicles because of incomplete combustion of fuel. CO emissions are a significant concern because they can be harmful to human health. When breathed in, CO enters the bloodstream and reduces the amount of oxygen that can be transported by red blood cells. This can lead to symptoms such as headache dizziness, nausea, confusion, and even death in several cases.

CO emissions from vehicles can be reduced through a variety of measures. One key strategy is to ensure that vehicles are properly maintained, which can help ensure that the engine is running efficiently and produces less CO. Another strategy is to improve engine design, such as by using fuel injection systems that can precisely control the amount of fuel that is burned during each cycle. Catalytic converters, which are commonly used in modern vehicles, can also help to reduce CO emissions by converting CO into less harmful gases.

3.Carbon dioxide (CO₂) - Carbon dioxide is a greenhouse gas that is emitted from vehicles as a byproduct of burning fossil fuels such as gasoline and diesel. CO₂ emissions are a major contributor to climate change, as they trap heat in the Earth's atmosphere and contribute to global warming. Vehicles are a significant source of CO₂ emissions, accounting for a substantial portion of the total emissions from the transportation sector. To address this issue, many countries have established emissions standards for new vehicles that include limits on CO₂ emissions. These standards encourage automakers to develop and produce vehicles that are more fuel- efficient, which can help to reduce CO₂ emissions from the transportation sector.

Steps to reduce the CO_2 emissions from transportation, such as by driving less, carpooling, or using public transportation, choosing more fuel-efficient vehicles, and maintaining their vehicles properly to ensure they are running efficiently. These efforts are part of a broader effort to address climate change and reduce greenhouse gas emissions to prevent the most severe impacts of global warming.

4.Nitrogen oxides (NO_x) - Nitrogen oxides (NO_x) are a family of gases that are emitted from vehicles because of high-temperature combustion in the engine. The main components of are nitric oxide (NO) and nitrogen dioxide (NO₂). NO_x emissions are a major contributor to air pollution and can have negative impacts on human health and the environment. NO_x emissions contribute to the formation of ground-level ozone and smog, which can cause respiratory problems and aggravate asthma. NO_x emissions can also contribute to acid rain and eutrophication of water bodies, which can have negative impacts on ecosystems. [2]

To reduce NO_X emissions from vehicles, many countries have established emission standards for new vehicles that include limits on NO_X emissions. These standards require that vehicles use technologies such as exhaust gas recirculation, lean-burn engines, and selective catalytic reduction to reduce NO_X emissions. Additionally, regular maintenance of vehicles, such as ensuring that engines are tuned up and running efficiently, can also help to reduce NO_X emission.

Formation of Nitrogen Oxide (NOx)

 NO_X has an adverse effect on the respiratory system. This causes inflammation in the airways of the respiratory system resulting in decrease in lung function, infections and increase in response to allergens. Not only health, high amount of NO_X is also responsible for damaging the environment. The vegetation becomes more prone to disease and frost damage. This makes the leaves damage, and the growth of the plants gets reduced. NO_X reacts with other pollutants in the presence of sunlight, forming ozone which is very harmful for the vegetation. Majority of NO_X is produced by the road transportation vehicles, railways, and airways,



Figure 2 Main sources of No_x [2]

 NO_X is formed at higher temperatures, more than 1800K, where oxygen and nitrogen dissociate into their atomic state. This has been shown by Zeldovich extended mechanism in three equations.

$$N_2 + O = NO + N$$
$$N + O_2 = NO + O$$
$$N + OH = NO + H$$

The formation of NO is given by Zeldovich equations. Similarly, NO₂ is also considered harmful which is released from the exhaust from diesel engines. NO₂ is formed from NO at high temperature in the flame region. The formation of NO₂ is shown below.[3]

$$NO + H_2O = NO_2 + OH$$
$$NO_2 + O = NO + O_2$$

In the second equation, NO_2 is dissociated to NO in presence of atomic oxygen due to local quenching and cooling. Higher temperature and presence of oxygen are the key factors for formation of NO. Mostly, rate of formation of NO_X happens at the kinetic phase of combustion where the mixing of air and fuel takes place triggering combustion rapidly and thus, resulting in high temperature. Similarly, due to longer combustion duration, there is formation of NO_X but in higher concentrations with respect to the high temperature condition.

5. Particulate Matter & Diesel Soot Particle



Figure 3 Size distribution of particulate matter [3]

Particulate Matters are the pollutants which are composed of particles with various sizes and chemical compositions. There is a broad classification of particulate matter for their different sizes. The sizes are divided into two different categories- PM_{10} and $PM_{2.5}$. Particles with size diameter 10µm or smaller referred to as aerodynamic diameter are categorized as PM_{10} and particles with size diameter 2.5µm or smaller are categorized as $PM_{2.5}$. PM_{10} and $PM_{2.5}$ are very fine particles which can be inhaled. Details about the sizes and classifications are provided in the figure.

Soot particles are the pollutants from diesel engines for which it is termed as diesel soot particles. These are formed at a temperature of 1000K to 2500K with pressure of 50atm to 100atm in presence of sufficient air for complete burning of fuel. Formation of soot happens in four phases- nucleation, growth, agglomeration and adsorption and condensation. [3]



Figure 4 Phases of formation of diesel soot particles [3]

In nucleation phase, the condensed materials from the fuel are produced by oxidation or pyrolysis products, mainly composed of unsaturated hydrocarbons and polycyclic aromatic hydrocarbons. This reaction generates the smallest recognizable particle of size diameter less than 2nm, referred to as nuclei. Next is the growth phase, where the particle size increases. In this phase, the size of solid carbon core increases forming concentric shells. Then occurs agglomeration phase, where cluster formation of carbon molecules takes place. This happens due to interparticle collision leading to coagulation of the molecules resulting in increased size but decreased number of particles as they get connected to form a sphere. In the final phase, adsorption, and condensation phase, Un burnt Hydrocarbons gets adsorbed on the solid carbon cluster due to chemical forces or physical forces. These Un burnt Hydrocarbons comes from unburnt fuel that are trapped in the crevices of the compression ring which gets back into the engine cylinder in expansion stoke, and from cylinder oil film where the flame cannot reach which is termed as flame quenching. Then condensation occurs in exhaust stroke when the vapor pressure of hydrocarbons exceeds its saturated vapor pressure.[3]

2.2 Methods of Reduction of Pollutants

Pollutants formed inside the Cylinder.

The main factors for production of NO_X are combustion temperature and combustion duration time and availability of oxygen. Reducing the peak temperature decreases the amount of NO_X formation which eventually affects the rate of reaction and formation of other pollutants like CO and UHC. Some techniques like Low Temperature Combustion (LTC), Homogeneous Charge Compression Ignition (HCCI), Reaction Controlled Compression Ignition (RCCI) and Premixed Charged Compression Ignition (PCCI) were developed by research and experiments on engines to reduce, NO_X, CO and UHC. Another way is by introducing Exhaust Gas Recirculation (EGR) inside the engine which decreases the in- cylinder temperature, hence reducing NO_X formation but increases other pollutants like CO and HC.[3]

Using Exhaust after-treatment devices.

Lean NOx Trap (LNT) – the catalyst plays a vital role in the reduction of NO_x. This catalyst has three main components- first is noble metals like Platinum, Rhodium and Palladium performs oxidation and reduction reactions, second is Barium Oxide for NO_x storage and the third is support which is the surface area composed of oxides. Platinum oxidizes NO to NO₂ which are stored and reduced to N₂. Hence it is a type of emission

control technology used in internal combustion engines to reduce the amount of nitrogen oxides (NOx) in exhaust gases. The LNT works by absorbing NOx from the exhaust gas when the engine is running in lean-burn conditions, which means there is an excess of oxygen in the combustion chamber. The NOx is then stored in the LNT material, which is typically made of a combination of metal oxides, such as barium and cerium, supported on a high-surface-area substrate, such as alumina. When the engine switches to a richer fuel mixture, the LNT is heated to release the stored NOx and convert it into nitrogen gas (N₂) and oxygen (O₂). This process is known as regeneration, and it typically occurs automatically during normal driving conditions. LNT technology is particularly useful for reducing NOx emissions in diesel engines, which are often run in lean-burn mode to improve fuel efficiency. LNT systems can also be combined with other emission control technologies, such as diesel particulate filters (DPF), to further reduce harmful pollutants in exhaust gases.[3]



Figure 5 LNT Mechanism [4]

Selective Catalyst Reduction (SCR) is an emission control device used in diesel engines to reduce the levels of nitrogen oxides (NOx) in exhaust gases. The SCR works by injecting a reducing agent, such as urea or ammonia, into the exhaust gas stream before it passes through the catalyst. The catalyst contains a special material, typically made of metal oxides, that reacts with the reducing agent to convert NOx into harmless nitrogen gas (N₂) and water (H₂O). This process is known as Selective Catalytic Reduction (SCR).

The urea or ammonia is typically stored in a separate tank in the vehicle and is metered into the exhaust gas stream using a dosing system. The dosing system ensures that the correct amount of reducing agent is injected into the exhaust gas stream to ensure optimal NOx reduction without producing excess ammonia slip, which can also be harmful to the environment. SRC technology is particularly effective at reducing NOx emissions from heavy-duty diesel engines, such as those used in trucks and buses. It is also used in some passenger cars with diesel engines to meet strict emission standards.

Converter (SCR), which reduces NO_X to N_2 by injection of water-urea solution where urea is converted to ammonia. Nowadays, SCR is a common exhaust after- treatment device used in diesel engines. The water-urea solution otherwise known as Diesel Exhaust Fluid (DEF) or Ad-blue which is injected in the exhaust gases gets decomposed to ammonia (NH₃) and later converts the exhaust gases to N_2 . Below are the chemical reactions of conversion.[5]

 $4NO + 3NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$ $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$

Exhaust-gas system with catalytic reduction of nitrogen oxides (SCR) 1 Diesel engine, 2 Temperature sensor, 3 Oxidation-type catalytic converter, 4 Injection nozzle for reducing agent, 5 NO_X sensor, 6 SCR catalytic converter, 7 NH₃ blocking catalytic converter, 8 NH₃ sensor, 9 Engine control unit, 10 Reducing agent pump, 11 Reducing agent tank, 12 Fill level sensor.



Figure 6 SCR System [3]

Diesel Particulate Filter

For reduction of particulate matter, one of the widely used exhaust after- treatment devices used in diesel engines is Diesel Particulate Filter (DPF) which is about 90% effective in trapping the particulate matter. DPF is a honeycomb structured filter which is fitted on or after catalytic converter that traps the particulate matter emitted from the exhaust of diesel engine. The operation of DPF requirement is that it operates at high temperatures for which it is mostly placed after the turbocharger. When there is excess amount of particulate matter in DPF causing a blockage inside, The ECU of the vehicle detects it and burns the excess amount of particulate matter to clear the filter by introducing post injection resulting in rise of the exhaust temperature. This is called the regeneration phase. During the regeneration phase, the number of nanoparticles is released which are very less compared to the amount of particulate matter released directly from the engine exhaust.

The DPF works by trapping and collecting PM, such as soot and ash, in a porous ceramic filter that is in the exhaust system. The filter has a honeycomb-like structure with many small channels that allow exhaust gases to pass through while trapping PM.

Over time, the trapped PM accumulates in the filter, which can lead to a buildup of backpressure in the exhaust system. To prevent this, the DPF periodically goes through a process known as regeneration, which burns off the trapped PM and reduces it to ash. Regeneration can be either passive, which occurs naturally during normal driving conditions, or active, which is initiated by the engine control system.

DPF technology is highly effective at reducing PM emissions from diesel engines, and it is widely used in both passenger cars and heavy-duty vehicles, such as trucks and buses. It is often combined with other emission control technologies, such as Selective Catalytic Reduction (SCR), further reduces harmful pollutants in exhaust gases.[6]



Figure 7 Diesel Particulate Filter [3]

Three Way Catalytic converter

A three-way catalytic converter (TWC) is a type of emissions control device that is commonly used in gasoline-powered vehicles to reduce the emissions of harmful pollutants such as nitrogen oxides (NO_X), carbon monoxide (CO), and hydrocarbons (HC). The TWC works by using a combination of precious metal catalysts, such as platinum, palladium, and rhodium, to convert the harmful pollutants into less harmful emissions. The catalysts are located on a ceramic honeycomb or metallic substrate inside the catalytic converter.

The TWC operates in three stages, hence the name "three-way." In the first stage, the converter oxidizes CO and HC emissions, converting them into carbon dioxide (CO₂) and water (H₂O). In the second stage, the converter reduces NO_X emissions by using the remaining oxygen in the exhaust to react with and convert NO_X to nitrogen (N₂) and oxygen (O₂). Finally, in the third stage, any remaining oxygen and pollutants are further oxidized, completing the conversion process.

The effectiveness of the TWC in reducing emissions depends on several factors, including the quality of the fuel being used, the condition of the engine and exhaust system, and the operating conditions of the vehicle. Regular maintenance of the vehicle, including routine inspections and replacing worn out parts, can help to ensure that the TWC is working properly and reducing emissions effectively. The TWC is a key component of emissions control systems in gasoline-powered vehicles. By converting harmful pollutants into less harmful emissions, the TWC helps to reduce air pollution and protect public health.[6]



Figure 8 Three-way catalytic converter [3]

2.3 Vehicles considered as High Emitters

High Emitters means vehicles that emit a significant number of pollutants, those are the vehicles that do not meet these standards and produce emissions beyond the permissible limits. particularly exhaust emissions that contribute to air pollution and environment degradation. High emitters can significantly contribute to poor air quality, smog formation and health issues in Urban areas by releasing pollutants like carbon monoxide, nitrogen oxides and particulate matter into the air. The cause of vehicles being a high emitter

<u>From Engine point of view</u> – Old Vehicles and those with outdated engine designs may lack exhaust after treatment systems there by pollutants are significantly higher in old cars than the new cars equipped with modern exhaust after treatment systems which helps in reducing the pollutants.

<u>Malfunction or tampering of Exhaust After treatment systems</u> – This can be the main reason for emitting a high number of pollutants is when there is a possibility of a malfunction or tampering of the exhaust after-treatment devices, vehicles with tampered or a faulty DPF could be emitting a significantly high number of particulate matters in several orders of Magnitude.

<u>Malfunctioning of Emission control system</u> – A Faulty emission control systems such as catalytic converters and exhaust gas recirculation system, malfunctioning of oxygen sensors, clogged air filters, or worn-out spark plugs are more likely to produce higher emissions.

<u>Vehicle age and maintenance</u> – Older vehicles are often less fuel-efficient and have less advanced emissions control systems compared to newer models. As vehicles age, their emission control systems may degrade, leading to higher emissions. Under maintaining the vehicle by not checking exhaust after treatment functioning.

<u>Tuning for higher performance</u> – using of emulators or tampering devices which are aftermarket products, to increase performance, fuel economy or even to decrease repairing and operation cost for example by blocking the exhaust recirculating tube, matching SCR with ECU or it can also be done with adjustments to the ad-blue and reagent tank gauges that show different level than the actual level, removing DPF or replacing the factory installed working DPF.

3. Emission related Legislations

3.1 Air Quality legislations for EU

Air Quality standards legislation is passed to keep the atmosphere that humans reside in as clean as possible without polluting it by imposing or having certain measures. If air quality gets deteriorated or polluted, it will have an adverse effect on Human Health causing respiratory issues, change in climatic conditions of the region and environment. In response to this, the EU has enforced legislation, setting the standards and limits for improvement of air quality and for better quality of living. Air Quality standards of certain pollutants are as follows .[7]

Pollutant	Concentration	Averaging	Permitted
		Period	exceedances each year
PM _{2.5}	$20\mu g/m^3$	1 year	-NA-
PM10	$50\mu g/m^3$	1 day	35
	$40\mu g/m^3$	1 year	-NA-
NO ₂	200μ g/m ³	1 hour	18
	$40\mu g/m^3$	1 year	-NA-

Table 1 Air quality standards for PM_{2.5}, PM₁₀, NO₂ [7]



Figure 9 - Annual Mean NO₂ concentrations in 2020[8]

The above figure shows the annual concentrations of NO₂ in the year 2020 for 33 countries. The annual limit set by EU was $40\mu g/m^3$ and the limit set by WHO was $10\mu g/m^3$. From the Figure 9 provided, it can be concluded that observed the countries exceeding above the EU limit which are presented in red are above $50\mu g/m^3$. Orange dots depict the countries whose limits were reasonable and were negligible with respect to the countries within the limit. According to the report from European Environment Agency (EEA), around 9 EU countries exceeded the annual limit value of NO₂ in the year 2020, although all the 33 countries whose data are interpreted here exceeded the WHO limit.[8]



Figure 10-Figure 10 - Annual mean PM2.5 concentration in 2020 [8]

The above figure shows the annual concentrations of $PM_{2.5}$ for the year 2020 for 27 countries. The annual limit for $PM_{2.5}$ set by EU was $25\mu g/m^3$ and the WHO recommended limit was $5\mu g/m^3$. It was observed that the countries exceeding the EU limit bearing red dots were comparatively less than the countries within the limit. As per the report by EEA, 4 countries including 2 EU countries exceeded the annual limit of $PM_{2.5}$, also all the 27 countries were above WHO limit. [8]



Figure 11- - Daily concentrations of PM10 in 2020[8]

The above figure 9, shows the daily concentrations of 90.4% of PM_{10} in the year 2020 for 37 countries. The daily limit of PM_{10} set by the EU was $50\mu g/m^3$. It was observed that countries exceeding the EU limit bearing red and pink dots were sharply recognizable than the countries under the limit. As per the report of EEA, 10 countries including 8 EU countries exceeded the daily limit of PM_{10} and 4 countries including 2 EU countries exceeded the annual limit. WHO has recommended limit of $15\mu g/m^3$ in 2020, and based on this limit, according to the data majority over 30 countries exceeded the limit.

The Report from the year 2020 was chosen here for a unique reason that reports in 2020 were depicting that the concentrations of NO₂, $PM_{2.5}$ and PM_{10} were lower, the reason being due to the restrictions imposed on movement during the outbreak of COVID-19 pandemic. [8]

3.2. Emission Standards

The European commission has set standards for emission of pollutants from the vehicle considering air pollution level which should be followed by the vehicle manufacturers. Below are the emission standards for heavy duty in g/kWh and light commercial vehicles in g/km. [9]

Store	Data	Test	CO	HC	NOx	PM	PN	Smoke
Stage	Date	1051		g/	kWh	1/kWh	1/m	
Euro I	$1992, \le 85 \text{ kW}$	ECE R-49	4.5	1.1	8	0.612		
	1992, > 85 kW		4.5	1.1	8	0.36		
Euro II	1996.1		4	1.1	7	0.25		
	1998.1		4	1.1	7	0.15		
Euro III	1999.10 EEV	ESC & ELP	1.5	0.25	2	0.02		0.15
Luio III	only	ESC & ELK						0.15
	2000.1		2.1	0.66	5	0.10		0.8
Euro IV	2005.1		1.5	0.46	3.5	0.02		0.5
Euro V	2008.1		1.5	0.46	2	0.02		0.5
Euro VI	2013.01	WHSC	1.5	0.13	0.4	0.01	8.0×10 ¹¹	

Table 2 EU standards for heavy-duty diesel engines in steady-state testing [8]

Table 3 EU standards for heavy-duty diesel and gasoline engines in transient testing [8]

Stage	Date	Test	CO	NMHC	CH4a	NOx	PM	PN		
				g/kWh						
Euro III	1999.10 EEV only		3	0.4	0.65	2	0.02	-		
	2000.1	ETC	5.45	0.78	1.6	5	0.16	-		
Euro IV	2005.1		4	0.55	1.1	3.5	0.03	-		
Euro V	2008.1		4	0.55	1.1	2	0.03	-		
Euro VI	2013.01	WHTC	4	0.16	0.5	0.46	0.01	6.0×10 ¹¹		

Stage	Date	СО	HC	HC+NOx	NOx	PM	PN		
Stage	Date		#/km						
Positive Ignition (Gasoline)									
Euro 1	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-	-		
Euro 2	1996.01	2.2	-	0.5	-	-	-		
Euro 3	2000.01	2.3	0.2	-	0.15	-	-		
Euro 4	2005.01	1	0.1	-	0.08	-	-		
Euro 5	2009.09	1	0.10	-	0.06	0.005	-		
Euro 6	2014.09	1	0.10	-	0.06	0.005	6.0×10 ¹¹		
Compression	n Ignition (Diesel)							
Euro 1	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)	-		
Euro 2, IDI	1996.01	1	-	0.7	-	0.08	-		
Euro 2, DI	1996.01	1	-	0.9	-	0.1	-		
Euro 3	2000.01	0.64	-	0.56	0.5	0.05	-		
Euro 4	2005.01	0.5	-	0.3	0.25	0.025	-		
Euro 5a	2009.09	0.5	-	0.23	0.18	0.005	-		
Euro 5b	2011.09	0.5	-	0.23	0.18	0.005	6.0×10^{11}		
Euro 6	2014.09	0.5	-	0.17	0.08	0.005	6.0×10^{11}		

Table 4 : EU standards for passenger cars [7]

	1									
Category	Stage	Date	CO	HC	HC+NOx	NOx	PM	PN		
	Stuge		g/km							
Compressi	on Ignition (D	iesel)			1	1				
N1, Class I	Euro 1	1994.1	2.72	-	0.97	-	0.14	-		
≤1305	Euro 2 IDI	1997.01	1	-	0.7	-	0.08	-		
kg										
	Euro 2 DI	1997.01	1	-	0.9	_	0.1	_		
	Euro 3	2000.01	0.64	-	0.56	0.5	0.05	-		
	Euro 4	2005.01	0.5	-	0.3	0.25	0.025	-		
	Euro 5a	2009.09	0.5	-	0.23	0.18	0.005	-		
	Euro 5b	2011.09	0.5	-	0.23	0.18	0.005	6.0×10 ¹¹		
	Euro 6	2014.09	0.5	-	0.17	0.08	0.005	6.0×10 ¹¹		
N1, Class II	Euro 1	1994.1	5.17	-	1.4	-	0.19	-		
1305- 1760 kg	Euro 2 IDI	1998.01	1.25	-	1	-	0.12	-		
0	Euro 2 DI	1998.01	1.25	-	1.3	-	0.14	_		
	Euro 3	2001.01	0.8	-	0.72	0.65	0.07	_		
	Euro 4	2006.01	0.63	-	0.39	0.33	0.04	-		
	Euro 5a	2010.09	0.63	-	0.295	0.235	0.005	_		
	Euro 5b	2011.09	0.63	-	0.295	0.235	0.005	6.0×10^{11}		
	Euro 6	2015.09	0.63	-	0.195	0.105	0.005	6.0×10^{11}		
N1, Class III	Euro 1	1994.1	6.9	-	1.7	-	0.25	-		
>1760 kg	Euro 2 IDI	1998.01	1.5	-	1.2	-	0.17	-		
	Euro 2 DI	1998.01	1.5	-	1.6	-	0.2	-		
	Euro 3	2001.01	0.95	-	0.86	0.78	0.1	-		
	Euro 4	2006.01	0.74	-	0.46	0.39	0.06	-		
	Euro 5a	2010.09	0.74	-	0.35	0.28	0.005	-		
	Euro 5b	2011.09	0.74	-	0.35	0.28	0.005	6.0×10 ¹¹		
	Euro 6	2015.09	0.74	-	0.215	0.125	0.005	6.0×10 ¹¹		
	Euro 5a	2010.09	0.74	-	0.35	0.28	0.005	-		
N2	Euro 5b	2011.09	0.74	-	0.35	0.28	0.005	6.0×10^{11}		
	Euro 6	2015.09	0.74	-	0.215	0.125	0.005	6.0×10^{11}		

Table 5 EU standard	s for Light commercia	l gasoline vehicles [7]
	8	8

According to the EURO 5 standards, L-category vehicles which includes vehicles like twoand three-wheel mopeds, two and three-wheel motorcycles, tricycles, and light and heavy quadricycles, The limit was set to 1000mg/km of CO, 100mg/km of total HC, 68mg/km of non- methane HC, 60mg/km of NO_X and 4.5mg/km of PM.

4. Detection of Excess Emitters.

Exhaust emissions from combustion-powered automobiles are harmful to both human health and the environment. Because of their recognized influence on health, the environment, and climate, NOx, and particulate matter (PM) emissions are of particular concern. NOx emissions continue to be a major issue, particularly in diesel-powered vehicles, where tampered and damaged vehicles contribute to excessive emission levels. A tiny percentage of vehicles (20%) known as High emitters, or automobiles that release pollutants beyond specific criteria, are generally connected with out-of-date or broken after treatment systems. These high emitters considerably contribute to road-based emissions, among all vehicles, the 1% of diesel vehicles release 18% of NOx; among heavy-duty vehicles, the 10% of high emitters account for 40% of PN and 20% of NOx emissions. [9]

It would be extremely advantageous to human health and the environment if these high emitting vehicles could be found and then kept to greatly cut emissions. Most present rules and legislations are only concerned with type approval procedures and do not consider deterioration of the exhaust after-treatment system defects that are not properly maintained and rectified or tampering of the exhaust after – treatment system that occurs over the usage of the vehicle over its lifetime. Because of newly implemented rules and documented health impacts on the human respiratory and cardiovascular systems, interest in real-world or real driving scenario emissions is being developed.

4.1 Tail pipe emission measurement

On Road tail pipe measuring test or Real-world Driving Emission testing, is a method used to assess a vehicle's actual emissions while it is being driven on the road, under real-world conditions. This type of Emission testing aims to provide a more real representation of a vehicle's emissions performance and to identify high emitters when compared to laboratory-based emission tests. This type of measurement is done by using portable emissions measuring systems (PEMS), where tail pipe measurement using PEMS is an onboard instrument that involves the real - time monitoring and analysis of vehicle exhaust emissions as the vehicle is under real – world conditions. Driving conditions could be acceleration, stop - and - go traffic or at Idle operation where a probe is inserted into the vehicle's exhaust pipe to collect a sample of the exhaust gas. This sample is then analyzed to determine the number of pollutants that are being emitted by the vehicle. The emission data can be compared to applicable emission standards and regulations to assess if the vehicle exhaust after treatment system is functional or tampered. PEMS collect continuous samples to calculate emission factors and are regarded as "standard methods" for measuring vehicle emissions which provide valuable data to emission regulation agencies to detect defective vehicles which is known as Periodic Technical Inspection of vehicle emissions which is by assessing the exhaust emissions of vehicles to ensure they meet regulatory standards for air quality. The primary goal of the Emission inspections is to identify vehicles emitting excessive pollutants on the road. If a vehicle fails to meet the regulatory standard, the owner of the vehicle is required to have the vehicle repaired and retested which encourages maintenance practices that reduce emissions and contribute to cleaner air.

One such method is the non-volatile particle Test (nvPN) which is a measurement technique used to assess the concentration of particles that are not affected by evaporation during the measurement process at idle. When exhaust particles are subjected to high temperature, volatile components such as water or organic compounds may evaporate which can alter the particle size and composition. To avoid this, non-volatile particle number measurements are carried out at elevated temperatures to minimize the effect of Evaporation. General procedure on how a non-volatile particle test is conducted.

<u>Collection of Sample</u> - A sample of the Exhaust plumes is drawn into the measurement instrument. This sample contains a mixture of particles of various sizes and compositions.

<u>Heating</u> – The collected particles are heated to a specific temperature, typically above the boiling point of the most volatile components. This heating process is necessity as it removes volatile components without altering the non-volatile particles.

<u>Measurement</u> – The instrument starts counting the number of particles that remain after the heating process. This count represents the non-volatile particle number concentration.

<u>Data Analysis</u> – The collected data can be analyzed to understand the distribution of nonvolatile particles in terms of sizes and concentrations, and it can be further used to calculate the emission factor of individual vehicles giving the results in $\#/cm^{3}$.

Nanomet3 is one of the measuring instruments which can be used to perform non-volatile particle number (nvPN) tests for the measurement of exhaust plumes from the vehicle. In this Experiment, the tail pipe measurement is done by Nanomet3.

4.2 Remote Sensing Method

Remote emission sensing (RES) is another method for identifying high emitters and screening real-world emissions from in-use cars. Remote Sensing method is a contactless emission testing method used to identify vehicles with high emission levels. Remote sensing methods can be used to assess and monitor vehicle emissions by analyzing the composition and characteristics of vehicle exhaust plumes. It provides a non - intrusive method to collect data on emissions from many Vehicles in real- world driving conditions. Vehicle emission remote sensing differs from all other regulatory emissions test methods in that the testing equipment does not physically interact with the vehicle undergoing testing. Rather, a light source and detector, placed either at the side of or above a roadway, are used to measure exhaust emissions remotely via spectroscopy as vehicles pass by the measurement location or by a probe which is placed in the position near the exhaust of the vehicles which passes preferably in the middle of the road or the corner. In this way, remote sensing measurements yield snapshots of emission rates from hundreds of individual vehicles as they are driven on actual roadways by their owners. Speed and acceleration are measured at the same time as the emissions measurement, providing information about the engine load. Finally, a camera captures an image of the vehicle's number plate, allowing for the retrieval of essential vehicle information for example, make, model, model year, certified emission standard, fuel type, rated power from vehicle registration databases. Thus, the ensemble of remote sensing measurements provides air pollutant emission rates for the fleet across a wide range of driving conditions. This data can be sorted by vehicle category (example by fuel and Euro standard), brand, possibly vehicle model, and eventually down to the level of individual vehicles, as much as the overall sample size allows.[10].

The pollutants from the exhaust of the vehicle that has just passed, as well as from the background presence of the species in the ambient air. Therefore, the pollutant concentration that was measured before the vehicle crossed is taken as background pollution and subtracted from the measurement. This difference is ascribed to the exhaust of the vehicle that has just passed by. Each valid record is the average of ten to 25 valid concentration measurements of the vehicle's passing. If certain quality parameters are met, the average concentration increment is retained. The same is done with the concentration of carbon dioxide (CO₂) in the plume. The CO₂ increment is directly proportional to the fuel burned in the engine of the vehicle, and thus to the amount of fuel consumed. CO₂ and air pollutants are subject to the same dilution and dispersion conditions, and hence it is meaningful to take their ratio. This ratio is the instantaneous emission rate expressed in units of grams pollutant emitted per kg of fuel burned for each vehicle measured. The instrument is regularly calibrated against a puff of gases of known concentrations. The second unit, a camera, records the number plate of the vehicle. Thus, technical data for the vehicle can later be accessed from the vehicle registration database. Most important are the certified emission standard or the year of first registration, the fuel type, the rated engine power, the gross vehicle weight, the vehicle makes and model. The emission rate can be determined in grams of pollutant per kilogram of fuel consumed at a certain engine load, for a vehicle whose technical characteristics are known from the vehicle's registration data.

Remote sensing is potentially the best option for:

- Determination of fleetwide emissions factors to assist local governments in policymaking decisions, such as the establishment of vehicle restriction measure such as low-emissions zones or vehicle bans, or the development of vehicle scrappage and renewal programs.
- Identification of high-emitting vehicle groups for market surveillance and followup regulatory compliance activities.
- Utilization of real-world vehicle emissions data to inform new customers of purchase decisions.
- It enables the identification of high-emitting vehicles, evaluation of the effectiveness of emission control programs, and monitoring of compliance with emission standards. By assessing emissions in real-world driving conditions, remote sensing complements laboratory-based emission testing and helps bridge the gap between regulated standards and actual on-road emissions.[10]

5. Measuring Instruments

Instruments that were used in this experiment were high-end portable devices which were carried in a point sampling van and were set up near the sampling point where the experiment was conducted. The instruments which were used for the experiment are as follows.

- a) For Point Sampling
 - 1. Engine Exhaust Particle Size (EEPS),
 - 2. Fourier Transform Infrared Spectrum (FTIR),
 - 3. NanoMet3 (nvPN).
- b) For Tail pipe measurement
 - 1. Non-Dispersive Infrared (NDIR)
 - 2. NanoMet3 (nvPN).

5.1 Engine Exhaust Particle Size Spectrometer (EEPS)

The Engine Exhaust Particle Size Spectrometer (EEPS) serves as a valuable instrument employed to measure and characterize the particle size distribution within engine exhaust emissions. Specifically designed to analyze the particulate matter (PM) emitted by internal combustion engines, such as those utilized in vehicles, aircraft, and industrial machinery, the EEPS plays a crucial role in understanding and evaluating engine exhaust particles. This instrument is used for the measurement of the lower concentration of exhaust particles in diluted exhaust. It is considered a fast-response and high-resolution instrument. It is manufactured by TSI Incorporated with a time resolution of 10 Hz. EEPS measures the size distribution and number of concentrations of exhaust samples.

Operating principle of EEPS

In this method, exhaust gas which are positively charged particles is fed continuously with the help of corona charger. The charged particles are then sent to high voltage electrode column which are transported down by HEPA filtered sheath air and then positive voltage is applied to the electrodes creating opposite charge with respect to particles which makes them repel outwards according to electrical mobility. This repel makes the particle strike electrometer in order – higher concentrations strike top electrometer and lower concentrations strike at the bottom electrometer. Electrometers are used for high sensitivity and for continuous measurement of particle sizes. For synchronizing the time delay between electrometers, variability in particle charge, image charge and size distribution with respect to time, EEPS has a built-in Digital Signal Processor (DSP)

1. <u>Aerosol Sample Inlet</u>: Equipped with an inlet system, the EEPS collects a representative sample of the engine exhaust. This system may incorporate filters or other devices to eliminate large particles or contaminants before the particles enter the spectrometer.

2. <u>Particle Charger</u>: The sample particles pass through a corona charger, where they acquire an electric charge. Typically, a corona discharge device generates ions to effectively charge the particles.

3. <u>Differential Mobility Analyzer (DMA)</u>: As a vital component, the DMA segregates particles based on their electrical mobility. Consisting of two electrodes, a sheath flow, and a classified aerosol flow, the DMA applies an electric field that induces particles of varying sizes to migrate at different rates, facilitating size segregation.

4.<u>Particle Detector</u>: Once the particles pass through the DMA, they are commonly detected by a particle counter or a condensation particle counter (CPC). These detectors measure the number of particles within specific size ranges and provide valuable insights into the particle size distribution.

5.<u>Data Analysis and Software</u>: The EEPS is linked to a computer or a data acquisition system responsible for collecting and analyzing data on the particle size distribution.

Specialized software processes the signals obtained from the particle detector, generating informative size distribution graphs or data tables.[11]



Figure 12 Schematic diagram of EEPS operation [11]

5.2 Fourier Transform Infrared Spectrometer (FTIR)

This instrument is used for identification of a variety of chemical compounds by absorption of Infra-Red Spectra. This instrument is an optical measuring device which detects compounds by absorption of light by the individual compounds. The FTIRs used were assembled in the respective university. Compounds like HC, CO, CO₂, and NO are detected by this instrument.

Operating Principle of FTIR

FTIR works on the basic concept of gases absorbing light of different wavelengths. The IR spectra is obtained by Fourier Transform of light intensity. This is done by principle of superposition of two light beams of varying path length which is passed through an optical cell with sampled gas. The molecular bonds of the compound vibrate in different frequencies and this light energy absorption excites the molecules. Molecular structure which is the difference between the initial state and excited state is given by the wavelength of light absorbed by the sample.

The operational process of the FTIR spectrometer involves the transmission of infrared light through the sample, subsequently gauging the extent of light absorption at each specific wavelength. This instrument comprises several crucial components that contribute to its functionality:

1. Infrared Source: Emitting a wide range of infrared radiation, typically from a heated filament or a silicon carbide rod, the infrared source generates infrared light across a diverse wavelength range.

2.<u>Interferometer</u>: Serving as the core component, the interferometer splits the incoming infrared beam into two distinct paths: the sample beam and the reference beam. Common types of interferometers utilized in FTIR spectrometers include Michelson and Fourier transform interferometers.

3. <u>Beam-splitter</u>: Employed to divide the incoming infrared beam into the sample and reference beams, the beam-splitter generally consists of a partially reflective mirror, facilitating the passage of both beams.

4. <u>Sample Compartment</u>: Designed to hold the sample being analyzed, the sample compartment accommodates solids, liquids, or gases. Within this compartment, the sample interacts with the infrared beam, and subsequently, the resulting absorption spectrum is measured.

5.<u>Detector</u>: Responsible for quantifying the intensity of the infrared light post-sample and reference beam traversal, detectors commonly employed in FTIR spectrometers encompass pyroelectric detectors and mercury cadmium telluride (MCT) detectors.

6. <u>Computer and Software</u>: By converting the detector signal into a digital format, the computer utilizes Fourier transformation algorithms to process the data. The accompanying software performs comprehensive data analysis and generates a spectrum representing the absorption of infrared light by the sample at distinct wavelengths.

FTIR spectrometers enjoy widespread use in various scientific and industrial domains. Their applications encompass the identification and quantification of organic and inorganic compounds, determination of molecular structures, and analysis of functional groups present within a given sample. Chemistry, pharmaceuticals, materials science, forensics, environmental monitoring, and numerous other fields benefit from the utilization of FTIR spectrometers.[12]



Figure 13 schematic of working of FTIR [12]

5.3 Non – Dispersive Infrared Gas Analyzer (NDIR)

A Non - Dispersive Infrared (NDIR) gas analyzer is a sophisticated instrument used for gas detection and measurement. It operates on the principle of infrared absorption to accurately determine the concentration of a specific gas in each sample. These analyzers find wide application in industries, environmental studies, and laboratories to monitor gases in the atmosphere or enclosed spaces.

NDIR gas analyzer and its essential components:

1. <u>Infrared Light Source</u>: The analyzer employs an infrared light source that emits specific wavelengths. The choice of wavelength depends on the gas being analyzed, as different gases exhibit characteristic absorption bands in the infrared spectrum.

2. <u>Gas Sample Chamber</u>: A chamber allows the gas sample to pass through, exposing it to the emitted infrared light. The gas in the sample selectively absorbs certain wavelengths of the infrared light based on its molecular composition.

3. <u>Detector</u>: The analyzer features a detector responsible for measuring the intensity of infrared light passing through the gas sample. The amount of light absorbed directly corresponds to the concentration of the target gas.

4. <u>Reference Detector</u>: To ensure accuracy and compensate for any fluctuations in the light source, many NDIR gas analyzers come equipped with a reference detector. This reference detector measures the intensity of infrared light that bypasses the gas sample, allowing for corrections when analyzing the signals.

5. <u>Signal Processing and Display</u>: Once the detector and reference detector provide their readings, the NDIR gas analyzer processes the signals to calculate the gas concentration. The results are then displayed on a screen or output through various communication interfaces.

The benefits of using NDIR gas analyzers include:

1. <u>High Sensitivity</u>: These analyzers can detect even trace amounts of gases, making them suitable for applications where low concentrations need precise measurement.

2.<u>Selectivity</u>: NDIR analyzers exhibit high selectivity for specific gases, reducing the impact of interference from other gases present in the sample.

3.<u>Real-time Monitoring</u>: Real-time data provided by NDIR analyzers allows for immediate detection of gas leaks or changes in gas concentrations.

4. <u>Low Maintenance</u>: Thanks to their lack of moving parts and long-lasting light sources, NDIR analyzers require minimal maintenance efforts. NDIR gas analyzers find widespread use in monitoring greenhouse gases like carbon dioxide (CO₂), hydrocarbons, methane (CH₄), carbon monoxide (CO), nitrogen oxides (NOx), and numerous other gases across various industries, including environmental monitoring, industrial safety, process control, and emissions monitoring.



5.4 Portable Emissions Measurement System (PEMS)

Figure 14 Portable Emission Measurement System [13]

PEMS, which stands for "Portable Emissions Measurement System," is a specialized tool used to analyze and measure the emissions produced by vehicles like cars, trucks, and buses while

they are being driven on the road. Its primary purpose is to assess compliance with emissions regulations and provide a better understanding of a vehicle's real-world emissions under different driving conditions.

Unlike conventional laboratory testing, where vehicles are measured on a dynamometer, PEMS allows researchers and regulators to gather emissions data in real-world scenarios. This means that the equipment can capture a more accurate and comprehensive picture of a vehicle's emissions performance, considering various factors such as driving speeds, accelerations, and loads. The PEMS equipment is equipped with sensors that measure exhaust gases, particulate matter, and other pollutants, and it also includes a data logging system to record the collected information. This data is then used to evaluate the environmental impact of vehicles and ensure they meet emission standards set by government authorities. The use of PEMS provides valuable insights into a vehicle's real-world emissions, enabling researchers and policymakers to make informed decisions in their efforts to reduce air pollution and improve air quality. Additionally, it offers automakers an opportunity to optimize their vehicle designs and emissions control systems to meet stringent environmental standards. [13]

5.5 Nanomet3 (NM3)

Nanomet3 is a non-volatile particle number counter instrument, which works by the principle of electrical charging measures the concentration and size distribution of exhaust plumes by measuring only the solid nonvolatile solid particle fraction that do not evaporate at high temperature or change their characteristics during the measurement process. Non-volatile particles are those that remain stable in terms of size and composition under the conditions of the measurement.

Operating principle.

<u>Sampling and Aerosol inlet</u> – The instrument draws in a sample of the exhaust plumes containing particles of various sizes. The sample is directed through an inlet system that helps conditioning of the sample and is passed through the instrument.

<u>Particle Detection</u> – within the instrument, particles pass through a detection zone where their properties are analyzed. The instrument works on the principle of electrical mobility

principle where particles are exposed to an electric field, depending on their size and charge, particles move at different speeds within the field. The time it takes for a particle to traverse a known distance provides information about its size.

<u>Data Analysis and Classification</u> – as particles are detected and their properties are measured, the NM3 classifies them into different size bins or ranges, this allows the creation of size distribution profile of the particles in the sample.

<u>Nonvolatile particle selection</u> – it is operated at temperature that prevents the evaporation of particles that do not undergo significant volatility. This helps ensure that the measurements accurately represent non – volatile particles.

<u>Output</u> – the instrument provides data output in the form of particle concentration per unit volume and the size distribution graphically or numerically.

6.Objective

The goal of this thesis is to analyze data from remote sensing measurement and conventional tail pipe measurement to detect high emitting passages for the test vehicles due to malfunction, wear or tampering and to validate the results. The validation is to be conducted by passage of vehicles with known emissions characteristics through roadside measurement point and by tailpipe tests of selected vehicles , by which the analyzed data could give information regarding the ability to discern between vehicles with and without a functional diesel particle filter, Emission factors of each individual vehicles that had passed are to be calculated per kg of fuel based on NO/CO₂ and PN/CO₂ and CO/ CO₂ ratios which are determined by linear regression method. Considering Emission factor, limit of quantification, high emitting vehicles are to be identified and further evaluate the data to determine the suitability of instruments, sampling location and vehicle spacing in real driving environment by remote sensing method and to compare and validate the results with Conventional tail pipe measurement system.

7.Experimental Setup

The experiment was carried out in the Entrance gate premises of Czech University of Life Sciences Campus in Kamycka street in Prague on 20th of October 2022 measuring the vehicles entering the university premises being the primary Experiment. A small set of Experiment also was carried out on 1st of July 2023, in the same location in Prague. The Project - Campaign was conducted collaborating with City Air Remote Emissions Sensing (CARES). The Instruments which were used are from two universities, Czech Technical University (CTU) and Czech University of Life Sciences were used and also from the CARES Project.

The main components of the experimental setup are described below:

1. Selection of Sampling site

It is necessary to place the sampling line in the right location from where the exhaust samples from the vehicles can be collected correctly know the concentrations of the pollutants. The purpose of selecting this Sampling point as the location for measuring is that, for the vehicles to enter the university the vehicles must produce a registered card from the university there by which the license number of the vehicle is registered in the data and the vehicle is identified easily. Furthermore, this process gives a time window to measure and note the emissions by FTIR and EEPS and tail pipe measurement of 10 seconds based on request to the owner of the vehicles.

2. <u>Vehicle Detection and license plate recognition</u>

The exact passing time of the vehicles is of great significance for automated postprocessing. This is especially the case if several vehicles pass by the measurement location, and they have only a small spacing between them. The exact passing time is required during data post-processing to resolve the different plumes correctly and hence the camera is placed to recognize and capture vehicle registration plate and the time of passing. Vehicle Registration is used to obtain Vehicle technical data for further investigation if required.

Automated number plate recognition (ANPR) systems are commonly used for license plate detection. The performance of the ANPR camera must be monitored since numerous things might influence it [19]. License plates might get dirty particularly in the winter or when it is raining, and the ANPR camera may be unable to identify all the plates of the passing cars especially if they pass at short intervals as it blocks the camera's Point of View. This complicates data post-processing and emphasizes the significance of good vehicle pass recognition.

3. Emission Measurement

The experimental setup was placed inside a Portable Van on the side of the Gate premises where the owners of the vehicle had to present the registration card and then are allowed to pass through the gate enter, meantime EEPS and FTIR instruments measures the Exhaust plumes emitted by the vehicles were recorded and noted down in the data base. [figure -16] depicts the Sampling site location.

The measurement is usually performed with a tube like structure which collects the diluted exhaust from the passing vehicles The position of the sample collecting tube can be placed either in the middle of the road by placing the tube directly on the road over which the vehicles pass or on the side of the road because the position of the sampling collecting tube has an influence on the measured Exhaust Plumes, the closer the tube is to the position of exhaust of the vehicles, lesser is the dilution of the measured plumes which is a necessity.

The conventional tail pipe measurement was done on selected vehicles to extract the information regarding the number of particles which were emitted from a specific vehicle passing through the location of the experimental Setup by NDIR, nvPN Nanomet3 Instrument. The measuring Probe from the Instrument is inserted into the Exhaust pipes of the vehicles, and it is recorded for further analysis.

Any indication of High emitting vehicle depicts that either due to tampering of exhaust treatment devices or an identification of non-stochiometric air-fuel ratio, were noted down for further analysis. On the day of the experiment, there were over 526 cars which had passed the sampling point, out of which in this experiment, it was possible to measure 457 vehicles with point sampling during the experiment, which was carried out on October 20th, 2022, for out of which selected 47 vehicles were measured with a short 10 - seconds tail pipe measurement was carried out and the data from both type of measurement were recorded and saved in the data acquisition for further analysis. selected 29 vehicles on 1st July 2023 were measured following the same procedure.

The main aim of the experiment was to compare and validate the data of the measured vehicles from Remote sensing method using Engine Exhaust Particle Size (EEPS) and Fourier Transform Infrared Spectrum (FTIR) with conventional stationary tail pipe measurement, which is PEMS, using Non-Dispersive Infrared (NDIR), NanoMet3 (nvPN).



Figure 15 Instrument setup



Figure 16 Sampling point - vehicle moving [14]



Figure 17 Sampling point - vehicle plumes measurement [14]



Figure 18 Tailpipe measurement [15]



Figure 19 Additional tailpipe measurement and diagnosis.[15]

8. Analysis

After the measurement was completed, the analysis of the data, calculation of Emission factor, and comparison of data is carried out. For a case, from the measured data of particles and CO2 with respect to time, a time bracket from 10.33.30am to 12.00.00pm is considered from the data measured on 20.10.2022, which can be seen in the figure to understand the signal readings of high emitters, low emitters, and background noise. From the Figure 21,

- 1 High Emitter strong signal This peak of PN which is from vehicle bearing a registration 2BR81XX Renault had passed through the sampling point; this vehicle could be an example for a clear sign of high emitter at time 10.49.59am.
- 2 High Emitter Low Signal The smaller peak compared from the case the previous case at 10.49.59am, this peak at 11.05.02am is from a vehicle bearing registration 6E813XX which passed through the sampling point.

- 3- Clean Vehicle Signal This peak at 11.17.24 is from a vehicle bearing registration 5SX21XX which passed through the sampling point which can be considered as Low emitter signal.
- 4 PN noise signal This region marked on the picture depicts that there was no passage of vehicles passing through, so it is nothing but the background concentration or the noise.
- 5 CO2 and PN peaks signals generated due to passage of vehicles the peaks are higher than the background from the time from 11.45.00 to 11.52.00am, at least 6 vehicles have passed the sampling point shows the peaks clustered in this time duration.



Figure 20 - Graph depicting Measurement by Remote Sensing Method.

8.1. Background concentrations

Estimation of background concentrations is important in a road-side emission measurement because of frequent change in background with respect to time. This change in background happens due to the following reasons.

- The impact of wind, which changes the dilution ratio.
- Interference of exhaust gases from passing vehicles.
- Change in concentration of gases.

Background concentrations could also be called the blank signals obtained during no passage of vehicles. The signals were carefully observed and was found that.

- The data obtained from the instruments were shifted due to presence of background concentrations.
- The peak time and settling time were different for different time limits. This could be due to wind speed and change in wind direction.
- The peak time was shorter than the settling time during the testing.

Peak time is the time in seconds to reach the peak point of the signal from steady state whereas, settling time is the time in seconds to reach steady state from peak point of signal. For correction to the background concentrations, a shift was used in the formulation depending on the rise of steady state signals. Background concentration is inevitable when the tests are conducted in an open environment like which is done in this experiment. In general, the net value of the signal can be calculated by removing estimated background from the recorded value. These background concentrations are often referred to as 'noise' or the 'disturbance' in the signal. Noise can be divided into two categories- one is Internal Noise which is associated with its own components; and the other is External Noise which is associated with the vibration or any physical disturbance to the instrument.

For Example, from the Figure 21, Considering the measurement which was carried out on 20.10.2022 during the bracket of time from 10.59.34 To 11.01.58am, as we can see there was no vehicle passing at this passage time, shown in the Figure 22, which is nothing but the background concentration.



Figure 21- Graph depicting Background noise from EEPS Measurement

8.2 Limit of Detection & Limit of Quantification

The smallest value from which it is statistically certain to infer the presence of concentration is referred to as the limit of detection (LOD). It is determined by measuring the signal response of blank samples (samples without the analyte). The LOD is typically expressed as a concentration or an amount, and a higher LOD indicates lower sensitivity [16].

Contrarily, a Limit of Quantification (LOQ) is the lowest concentration at which a measurement can be made with a fair degree of statistical certainty. It is determined by measuring the signal response of blank samples (samples without the analyte). The LOD is typically expressed as a concentration or an amount, and a higher LOD indicates lower sensitivity. The LOQ is typically higher than the LOD and ensures that the quantified result falls within an acceptable range of uncertainty.

Two forms of error must be considered when estimating LOD and LOQ:

Type I error - α , known as false positive error or error resulting from detecting something that is not there.

Type II error - β , known as false negative error or error resulting from detecting something that is there but was not detected.

The uncertainty of instruments is considered low and low value of error is selected. the values of α and β is selected as 5% = 0.05 respectively. LOD is numerically equal to 3 times the standard deviation of blank concentration or noise and considering accuracy and precision is kept constant around its range. Formula is given by LOD = 3 σ .

LOQ is numerically equal to 6 times the standard deviation of blank concentration or noise. the formula is given by LOQ=6 σ

where, σ is the standard deviation of blank concentrations from the time interval 10.59.34am to 11.01.58am. Since this experiment is carried out in an open atmosphere there will be a signal in the instrument because of blank concentrations by the presence of atmospheric air. The standard deviation of the blank signal which was taken into consideration from the time bracket 10.59.34 To 11.01.58am from the figure 21, which was taken into consideration where there was no passage of vehicles.[17]. LOD and LOQ calculated are calculated in the Table 5.

Instrume	nt	LOD	LOQ
EEPS	PN in #/cm ³	2089	4044
FTIR	CO2 in ppm	4	8
	CO in ppm	0.5	0.3
	NO in ppm	0.6	1.1

Table 5 LOD and LOQ me	easurement table
------------------------	------------------

8.3 Instrument Response time

Instrument Response time or Time Response can be defined as the time or duration it takes for a measurement to fully react and provide stable output after subjected to a change in the output signal or time in seconds which a signal of an instrument takes to go from an initial state say from 10% to new steady state say to 90% to 95% of its maximum absolute value. Response time is considered to understand the behavior of measurements from an Instrument which is a necessity in the field of measurements. The Response Time is calculated by giving a step change in the input signal of the instrument and wait for it to rise and have a stabilized output say in interval of 30 seconds to obtain the peak from base signal of 0% till the maximum peak of 100% is reached then calculate the time it takes for the outputs to reach the specified between 10% of peak T_{10} to 90% of peak T_{90} of the final value. The estimation is carried out for averaging four rise periods of signal of each instrument.

Table 6 Instrument time response of EEPS and FTIR

Instrument	FTIR	EEPS
Response time	1.8 seconds	1.8 seconds



Table 7 Instrument time response of EEPS and FTIR

Figure 22 Time response for FTIR in 5 Hz



Figure 23- Response time for EEPS in 5Hz

8.4 Instrument time resolution

Since the experiments were carried out on different days the major one on 22.10.2022 and followed by small set of Experiment on 01.07.2023, the instruments were used on both the days of experiment the frequencies of the instruments would be different. So, hence it is a necessity to synchronize the frequencies of the instruments to a same frequency by linear interpolation. FTIR was operating at 5Hz, EEPS instruments was operating at 10Hz and Nanomet3 has a reporting frequency of 1Hz. The frequencies of the instruments are resampled to 5Hz which is the lowest frequency obtainable from the instruments which helps to identify the concentration peaks which was measured easily and with a good resolution The table shows the frequencies of the instrument.

Instrument	Recorded	Frequency	Resampled
	(H	lz)	Frequency (Hz)
	20.10.2022	01.07.2023	
EEPS	10	10	5
FTIR	5	5	5

Table 8 Instrument frequency response

8.5 Calculations

8.5.1 Significance of PN/CO2 ratio.

To estimate the ratio of concentrations of NO to CO_2 , the ratio of concentrations of PN to CO_2 , the ratio of concentrations of CO to CO_2 , is done by linear Regression method where the concentrations of PN or other pollutants and the concentrations of CO_2 are correlated by the measured values. The slope factor obtained gives the ratio of the concentrations of pollutants with respect to concentrations of CO_2 from which the further calculation of Emission factors can be obtained by which one can estimate the number of pollutants is being released and distinguish any abnormality in the vehicle emission which could give information about high emitters. Linear regression is carried out for a specific time of the vehicle passage. The correlating

factor is an estimation of the level of correlation of particle concentrations with the concentrations of CO_2 which was measured or detected.

Assumed
$$EF_{NO} = \frac{NO}{CO_2} = \frac{Concentration of NO}{Concentration of CO_2}$$

Assumed $EF_{PN} = \frac{PN}{CO_2} = \frac{Concentration of PN}{Concentration of CO_2}$

concentration of NO in ppm and CO_2 in ppm, and concentration of PN is in #/ cm^{3.}

Considering the case for the calculation, on 20.10.2022 at time 12.30.45, a vehicle bearing the registration 5S1 42XX (Volkswagen – Diesel) was allowed to pass through the Experimental Site for which the calculations have been made in the following table.

The line regression method for calculating the slope factor PN/ CO₂ where slope is 2566.2, R^2 value is 0.98, which gives an idea how well it was correlated with the concentration of CO₂ by which the emission factor is calculated. R^2 – correlating factor is defined as the measure that indicates the proportion of the variance in the dependent variable that is explained by the independent variables in a linear regression. It quantifies how well the model fits the observed data points.



Figure 24 - Linear Regression - PN/CO2



Figure 25 - Graph depicting PN/CO2 regression by EEPS and NM3

	Volkswagen – 5S1 42XX								
Vehicle									
Date / Time		20	0.10.2022 / 12:3	0:45					
Cor	ncentrations of p	ollutants	Linear F	Regression					
	FTIR								
CO ₂ (ppm)	CO (ppm)	CO (ppm) NO (ppm) CO/CO2 NO/CO2							
39.15	0.22	0.22 0.53 0.008 0.003							
EEPS									
CO ₂ (ppm)	CO (ppm)	CO (ppm) PN (#/cm ³) CO/CO ₂ PN/CO ₂ EF _{PN} (#/kg _{fuel})							
39.15	0.22	0.22 127684 0.008 266762 4.00E+15							

Table 9 Emission factor calculation for a case on 20.10.2022

8.5.2 Calculation of Emission Factor

An emission factor refers to a numerical value that represents the quantity of a specific pollutant emitted per unit of activity or product. It's commonly expressed as the mass.

(In kilograms) of the pollutant released for each unit of distance travelled (in kilometers). Emission factors serve as essential tools in managing air quality, conducting environmental impact assessments. They enable policymakers and regulators of the emission board to estimate emissions without the need for direct measurements from each source. Instead, emissions can be estimated by multiplying activity data.

(For example fuel consumption) by the corresponding emission factor for a particular pollutant.

For the calculation of Emission Factor, certain parameters were considered.

- Carbon content in fuel is taken as be 0.862 for both diesel and gasoline.
- The presence of CO and CO₂ for both diesel and gasoline is considered.
- The molecular volume of gas is assumed as $22400 \text{ cm}^3/\text{mol}$.

The formula is given by.

$$EF_{NO} = \frac{m_{NO}}{m_{fuel}} = \frac{[C] * C_{NO} * M_{NO}}{M_{C} * C_{CO_2} * \left(1 + \frac{C_{CO}}{C_{CO_2}}\right)}$$
$$EF_{PN} = \frac{N_{PM}}{m_{fuel}} = \frac{[C] * V_m * C_{PN}}{M_C * C_{CO_2} * \left(1 + \frac{C_{CO}}{C_{CO_2}}\right)}$$

where,

EF_{NO} - Emission Factor of NO in g/kg_{fuel}

 EF_{PN} - Emission Factor of PM in $\#/kg_{fuel}$

C - Carbon content in Fuel = 0.862

C_{CO} - Concentration of CO measured from FTIR.

 C_{CO2} - CO_2 concentration measured from FTIR.

C_{NO} - Concentration of NO measured from FTIR

 C_{PN} - Concentration of PM measured from EEPS.

 V_m - Molecular Volume of gas = 22400cm³/mole

M_C - Molecular Weight of Carbon M_{NO} - Molecular Weight of NO

The molecular weight of carbon is 12g/mol and molecular weight of NO is 30.01g/mol in the molecular weight of NO₂ is 46g/mol is considered in the calculation as NO reacts with the atmospheric air to formNO₂.

The same case of Vehicle bearing the registration plate 5S1 42XX (Volkswagen – Diesel) which was allowed to pass through the Experimental Site at time 12.30.45 on 20.10.2022 for this calculation as well, considering the linear regression and slope factor obtained by the method, further calculation of emission factor of the vehicle in $\#/kg_{fuel}$ was calculated and is shown in the Table. Similarly, the Emission Factor in $\#/kg_{fuel}$ calculations for all the 457 vehicles are provided in Annexure Table 13.

Vehicle	Volkswagen – 5S1 42XX						
Date / Time	20.10.2022 / 12:30:45						
	Peak Concentrations Linear Regression						
	FTIR						
CO ₂ (ppm)	CO (ppm)	$EF_{NO}(g/kg_{fuel})$					
39.15	0.22	0.53	0.008	0.003	0.005		
EEPS							
CO ₂ (ppm)	CO (ppm) PN (#/cm ³) CO/CO ₂ PN/CO ₂ EF _{PN} (#/kg						
39.15	0.22	127684	0.008	266762	4.0E+15		

Table 10 - Emission factor calculation in $\#/kg_{fuel}$ for a case on 20.10.2020

8.5.3 Deriving of g/kg of fuel or #/kg of fuel to g/km or #/km

Emission Factor calculation for the vehicle in terms of g/km for pollutants which are gases and #/km for particulate matter, certain assumptions is considered as the individual details as there was not much technical information regarding about the vehicles which were measured.

Considering a case of Vehicle bearing the registration plate 5S1 42XX (Volkswagen – Diesel) which was allowed to pass through the Experimental Site at time 12.30.45 on 20.10.2022 for this calculation, The emission factor in #/km is calculated as shown in the Table. For Further 457 vehicles, the emission factor in #/km is calculated and tabulated in the Table in the Annexure Table 13.

Assumptions,

- The Density of gasoline fuel 0.755 kg/l
- The Density of diesel fuel- 0.85 kg/l
- Fuel consumption of the vehicle in l/100km

$$EF\left(\frac{g}{km}\right) = \frac{EF\left(\frac{g}{kg_{fuel}}\right)}{100} * FC * D_{fuel}$$
$$EF\left(\frac{\#}{km}\right) = \frac{EF\left(\frac{\#}{kg_{fuel}}\right)}{100} * FC * D_{fuel}$$

$$\label{eq:FC-Fuel} \begin{split} FC-Fuel \ consumption \ in \ the \ range \ 7.51/100 km \\ D_{fuel}-Density \ of \ Fuel \ assuming \ 0.85 kg/l \ for \ normal \ acceleration \end{split}$$

Vehicle Volkswagen – 5S1 42XX Date / Time 24.10.2022 / 12:30:45 FTIR NO (ppm) EFNO (g/kg of fuel) EFNO (g/km) 0.53 0.005 0.0024 EEPS PN $(\#/cm^3)$ EFPN (#/kg of fuel) EFPN (#/km) 127684 4.0E+15 1.92E+14

Table 11 Emission factor calculation in #/km for a case on 20.10.2020

9. Results and Discussion

9.1 Tabulation of Measurements.

For the selected 47 vehicles, tail pipe measurements which was measured in the form of #/cm3 from nvPN and readily available remote sensing measurement calculated in the form of Emission Factor in #/kg of fuel from the Remote sensing method and recalculated to Emission factor in #/km. Table 12 depicts tail pipe measurement, information regarding the registration of the Vehicle, type of fuel, and the time of passing and calculated emission factors in #/kg of fuel and in #/km which was measured on 20.10.2022.

Time	Vehicle Registration	Tail Pipe Tests in #/ cm ³	Emission Factor in #/kg of fuel (EEPS)	Emission Factor in #/km	Emission Factor in #/kg of fuel (nanomet3)	Type of fuel
12:13:59	8AF 26XX	2.0E+04	1.7E+13	8.2E+11	2.1E+11	Diesel
12:14:02	4AX 18XX	1.0E+03	5.2E+12	2.5E+11	9.1E+11	Gasoline
12:16:42	8AM 38XX	4.0E+03	6.6E+09	3.1E+08	3.9E+07	Diesel
12:18:44	4AF 02XX	7.0E+05	2.6E+14	1.2E+13	8.4E+13	Diesel
12:23:32	8AU 60XX	4.0E+03	2.8E+12	1.3E+11	2.1E+10	Diesel
12:23:29	3P8 94XX	2.0E+04	1.0E+12	4.8E+10	4.5E+11	Diesel
12:30:45	5S1 42XX	5.0E+06	4.0E+15	1.9E+14	8.0E+14	NA
12:34:35	3AY 20XX	2.0E+04	2.3E+12	1.1E+11	2.0E+11	Diesel
12:42:01	6AF 48XX	2.0E+03	7.9E+14	3.7E+13	1.9E+13	Gasoline
12:52:41	7AS 44XX	2.0E+03	5.7E+12	2.7E+11	8.3E+08	Diesel
12:52:06	4K7 47XX	1.0E+04	1.8E+12	8.6E+13	1.5E+11	Diesel
12:54:53	8P3 75XX	1.0E+03	1.4E+13	6.7E+11	2.7E+12	Gasoline
12:57:56	2E9 19XX	5.0E+06	3.7E+15	1.7E+14	3.1E+14	Gasoline
12:58:41	5J9 93XX	3.0E+03	2.7E+13	1.3E+15	2.9E+12	Gasoline
12:58:33	2A1 80XX	5.0E+04	9.9E+11	4.8E+13	8.6E+10	NA
13:00:37	2SB 27XX	5.0E+06	6.1E+16	2.9E+14	1.2E+15	Gasoline
13:00:53	8AM 70XX	5.0E+06	3.1E+15	1.5E+13	2.7E+14	Diesel
13:01:34	1TN 38XX	7.0E+03	1.0E+12	5.0E+13	1.5E+10	Gasoline
13:02:02	4AI 16XX	8.0E+02	1.5E+12	7.1E+13	9.2E+11	Diesel
13:02:48	9AC 26XX	5.0E+02	5.5E+10	2.7E+12	1.8E+09	Gasoline
13:08:52	6M2 87XX	2.0E+05	3.1E+14	1.5E+14	6.2E+10	NA

Table 12 Emission Factor Calculation for Measurement on 20/10/2022

13:11:35	4AN 27XX	5.0E+02	2.6E+11	1.2E+10	9.7E+10	Diesel
13:11:27	6E5 80XX	3.0E+03	3.7E+12	1.7E+11	4.2E+11	Gasoline
13:11:14	1SX 73XX	5.0E+03	4.3E+12	1.7E+11	4.9E+08	Diesel
13:13:09	4AR 93XX	3.0E+06	1.3E+12	6.4E+10	1.4E+08	Gasoline
13:13:44	3U9 94XX	5.0E+07	9.4E+15	4.5E+14	9.0E+14	Diesel
13:14:02	2AV 65XX	5.0E+06	2.8E+16	1.3E+15	5.5E+14	Gasoline
13:17:01	7AC 27XX	8.0E+02	2.7E+12	1.3E+11	4.3E+11	CNG
13:18:42	1AH 35XX	5.0E+06	4.2E+16	2.0E+15	3.5E+15	Diesel
15:26:45	7U4 55XX	5.0E+04	2.1E+12	1.0E+11	7.6E+09	Diesel
15:27:53	2SP 84XX	3.0E+04	3.3E+12	1.5E+11	6.2E+11	Diesel
15:30:54	3SH 55XX	3.0E+06	2.3E+12	1.1E+11	1.7E+11	Diesel
15:30:29	8AB 84XX	1.0E+04	5.2E+11	2.5E+10	2.6E+07	Gasoline
15:30:58	3SE 06XX	2.0E+04	1.7E+12	8.1E+10	2.0E+09	Gasoline
15:31:38	3AE 61XX	6.0E+03	3.4E+12	1.6E+11	6.8E+10	Gasoline
15:32:08	7AP 04XX	1.0E+04	2.6E+12	1.2E+11	2.8E+10	Diesel
15:32:31	4AN 24XX	1.0E+06	1.3E+15	6.2E+13	1.9E+14	Diesel
15:36:47	1UH 54XX	4.0E+06	3.2E+13	1.5E+12	5.0E+12	NA
15:38:03	8AM 64XX	3.0E+03	2.0E+12	9.6E+10	2.2E+11	Gasoline
15:39:12	5AX 05XX	5.0E+04	2.1E+12	1.1E+11	2.7E+08	Gasoline
15:39:55	7AF 02XX	8.0E+03	5.7E+12	2.7E+11	1.6E+11	Diesel
15:40:23	8AM 42XX	1.0E+04	1.6E+14	7.6E+11	5.2E+11	Diesel
15:41:09	5SA 39XX	2.0E+03	5.0E+10	2.4E+09	4.3E+09	Gasoline
16:00:25	5C7 27XX	2.0E+03	4.4E+11	2.1E+10	9.3E+09	Diesel
16:02:07	4ST 08XX	2.0E+03	1.6E+11	7.6E+09	1.0E+07	Diesel
16:03:02	6AM 71XX	5.0E+03	1.6E+12	7.6E+10	2.9E+11	Diesel
16:09:31	5AU 47XX	6.0E+04	4.3E+12	2.4E+11	1.2E+09	Diesel

For the selected 29 vehicles, tail pipe measurements which was measured in the form of #/cm3 from nvPN and readily available remote sensing measurement calculated in the form of Emission factor in Emission Factor in #/kg of fuel from the Remote sensing method The Table 13 depicts tail pipe measurement, as there was no information regarding the Vehicle, the time of passing of the vehicles is taken into consideration where the values showing higher than the background concentration meant passing of a vehicle and calculated emission factors in #/kg of fuel and in #/km which was measured on 01.07.2023.

Time	Tail Pipe Tests in #/ cm ³	Emission Factor in #/kg of fuel	Emission Factor in #/km	Emission Factor in #/kg of fuel (nanomet3)
10:02:19	1.6E+04	9.0E+10	4.3E+09	7.4E+09
10:02:52	1.4E+03	1.2E+12	5.7E+10	5.7E+10
10:03:07	5.6E+03	5.3E+11	2.5E+10	1.6E+10
10:04:21	7.0E+05	7.5E+12	3.6E+11	1.7E+09
10:04:56	4.2E+03	1.2E+13	5.7E+11	3.1E+11
10:05:48	1.7E+04	3.5E+11	1.6E+10	9.0E+10
10:06:07	5.0E+06	8.2E+15	3.9E+14	5.0E+14
10:06:34	1.9E+04	4.2E+11	2.0E+10	9.5E+10
10:09:07	1.8E+03	1.6E+13	7.6E+11	1.9E+12
10:12:56	1.6E+03	4.1E+15	1.9E+14	1.6E+14
10:16:18	4.0E+06	3.6E+12	1.7E+11	1.1E+11
10:18:59	5.0E+06	6.3E+14	3.0E+13	7.4E+13
10:22:11	6.6E+03	5.0E+12	2.4E+11	2.8E+09
10:26:31	8.0E+02	7.3E+11	3.5E+10	7.6E+11
10:31:32	5.0E+07	1.3E+16	6.2E+14	5.7E+15
10:33:02	2.0E+05	5.4E+12	2.5E+11	6.8E+11
10:33:27	5.0E+02	1.3E+11	6.2E+09	8.1E+08
10:33:48	2.6E+03	2.3E+12	1.1E+11	8.0E+11
10:43:06	4.9E+03	2.3E+12	1.1E+11	1.7E+10
10:44:39	2.8E+03	9.7E+13	4.6E+12	3.2E+12
10:57:50	4.0E+05	3.1E+12	1.4E+11	2.8E+09
10:58:32	5.0E+06	2.8E+16	1.3E+15	2.3E+14
10:59:16	8.0E+02	2.7E+12	1.3E+11	7.4E+11
10:59:33	1.0E+06	4.2E+13	2.0E+12	2.7E+12
11:00:03	5.0E+06	2.1E+12	1.0E+11	2.6E+11
11:00:56	3.2E+04	3.3E+12	1.6E+11	3.0E+11
11:01:19	3.0E+06	3.3E+14	1.6E+13	9.2E+13
11:03:24	1.0E+04	1.1E+15	5.3E+13	5.8E+14
11:04:48	6.0E+06	5.0E+15	2.4E+15	1.1E+14

Table 13 Emission Factor Calculation for Measurement on 01/07/2023

9.2 Observation

The goal of this experiment is to compare the measurements from two different methods of measurement which is conventional tail pipe measurement and Remote sensing method being the primary and detection of High emitters from the measured vehicles. Tail pipe measurements were carried out for 47 vehicles out of 457 vehicles on 20.10.2022 and for 29 vehicles for different fleet of vehicles on 01.07.2023. The measurement of tail pipe is in #/cm3.

For the measurements, the calculated Emission Factor in g/kg of fuel for high emitter detection or low emitter can be shortlisted based on

- By considering EURO standards, for vehicles according to vehicle type.
 Calculating Emission Factors in terms of EURO standard units [18] according to type of vehicle (Diesel or Gasoline).
- By considering and analyzing the calculated Slope Factors (ratio) and correlating factors (R²) for PN/CO₂ ratios by linear regression method.
- By considering the LOD and LOQ of pollutants and threshold limit of detection of concentration of CO₂.

Analysis is carried out with measurements with two different methods which is a scatter plot of emission factors of vehicles calculated remote sensing measurement on the Y- axis and Tail pipe measurements on the X-axis to have an idea about the vehicle emission range and group them into high emitters or low emitters.

From Table 12 and 13, the rows marked in yellow signify that they are high emitters. Blue colored rows signify that those vehicles could be a possibility of low emitters acting as temporary high emitters. The rows which are uncolored or white rows signify that they are low emitters. Information regarding the vehicle technical data were obtained from vehicle registry by the CARES.

Comparison between Remote sensing method and Tail pipe measurement method

From the 457 measured Vehicles in the sampling point, out of which 47 vehicles tail pipe measurements were done on 20.10.2020. Emission Factors were calculated for each of the selected tail pipe measured vehicles are analyzed with the two different methods of measuring and compared and to validate the acquired data shown in Table 12, the same procedure was followed for the measurement done on 01.07.2023 for 29 vehicles, measured with two different methods of measurement. Data shown in Table 13.

According to EURO Standards emission limit [18], Majority of the vehicles measured follow or under the limit which are in the range in and below emission factor being nvPN of 10^{13} #/kg of fuel [EF < 10^{13} #/kg of fuel] and nvPN tail pipe test under the range of < 10^5 #/cm³ these categories of vehicles can be grouped under the category Low emitters. From the Graph 26 for measurement on 20.10.2022 and Graph 27 for measurement done on 01.07.2023, which is a scattered plot or also known as cluster analysis of Emission of factors of the individual vehicles with respect to their tail pipe measurements, it can be clearly observed that all vehicles falling under the bracket of the green colored line depicts that these cluster can be grouped as Low emitters.

1.<u>For a case from 20.10.2022</u> - From Table 12, the vehicle bearing registration 7AS 44XX which passes the sampling point unit at 12:52:41pm is a good example for low emitters, as its emission factor is in range with the Euro standard limit. Although the Euro Limit [18] PN emission factor 6 x 10^{11} #/km for passenger cars, the limit here is set at EF < 10^{13} #/kg of fuel because this measurement is carried out in real road driving conditions, whereas the limit test is carried out in driving cycles not in real world road. The emission rate during idling is substantially lower than for other driving modes.[20]

2. For a case from 01. 07.2023 - From Table 13. A vehicle passing the sampling point at 11.01.19am is a good example of low emitter, since there is no information regarding the vehicle, passage time of the vehicle is taken into consideration, the vehicle measured nvPN tail pipe test under the range of

[$< 10^5$ #/cm³] and its calculated emission factor is of 10^{13} #/kg of fuel.

That is [$EF < 10^{13} \#/kg \text{ of fuel}$]

Similarly, it can be observed that there are countable number of vehicles whose range is above the emission factor being nvPN of 10^{13} #/kg of fuel [EF > 10^{13} #/kg of fuel] and nvPN tail pipe test over the range of > 10^5 #/cm³ and over, almost their range being an order of magnitude higher considering their NO Emission Factors being higher (from Annexure). This cluster of vehicles can be grouped as High Emitters which are marked as the points inside the red line depicted in graph 26 and in graph 27 and the high emitters are marked in yellow in Table 12 and Table 13.

1.<u>For a case from 20.10.2022</u> - from Table12, the vehicle bearing registration 2AV 65XX which passes the sampling point unit at 13:14:02pm is a good example for High emitter whose emission factor is in the order of 10^{16} #/kg of fuel and tail pipe measure which is over 10^{6} #/cm³, its emission factor is higher than the of magnitude above the range of Euro standard limit.

2.<u>For a case from 01.07.2023</u> - from Table13, the vehicle passing the sampling point unit at 10:58:32am is a good example for High emitter whose emission factor is in the order of 10^{16} #/kg of fuel and tail pipe measure which is over 10^{6} #/cm³, its Emission Factor is higher than the of magnitude above the range of Euro standard limit [18].

Vehicles distinguished as a high emitter could be of many different reasons from malfunctioning or tampering of a functioning and efficient DPF could be the reason, impaired EGR and emission control system. A small fraction of high emitters can influence a large fraction of total fleet emissions. Broken DPF double the fleet emissions, even if 1% of the total vehicle fleet has a tampered DPF, it emits 10x the normal range of Particulate matter emissions, which thereby increases fleet emissions by the order 10x [15]. Proper maintenance or inspection of an efficient DPF is a necessity for Diesel engines. for Example, 4AN24XX,

3U994XX and many marked as High Emitters from the Table 12 are diesel engines with a possibility of not having efficient or working or removal of DPF, in case of Vehicle 2AV65XX, 2SB27XX are identified as gasoline engines, which may have a defunct three way catalyst or impaired oxygen sensors or running on non-stochiometric air/fuel ratio on purpose for performance or by accident which is why regular inspection of functioning after exhaust system is a necessity, another case of vehicle being old 8AM7020 which was identified as a vehicle manufactured from 1980's where they lack or up to the mark of the modern exhaust after treatment devices.

Third group of Vehicles whose emission factors or tail measurement tests show higher values than the limits from one measuring method this could be a possibility of many reasons, measurement uncertainties being a reason, also it could be a possible case of 'Temporary High emitters', this behavior could be likely due to undergoing DPF regeneration process when it arrived to the university gate premises (Sampling point) from a highway which has higher speed limits where the Vehicles are at higher speeds which could have initiated DPF regeneration, if the regeneration process increases significantly, the engine would run slightly rich than stochiometric ratio, which can make low emitters as high emitters temporarily. Although before concluding, it is crucial to identify such vehicles for further inspection to exactly conclude why there was no satisfactory correlation between both the measurement methods and if it's a low emitter or low emitter acting as a temporary high emitter, or a high emitter where one of the measurement methods failed to distinguish it. Their range of emission factor is around $10^{14} - 10^{15}$ #/kg of fuel and tail pipe measurement range $10^5 - 10^6$ #/cm³

For a case from 20.10.2020 - From the Table12, the vehicle bearing registration 6AF 48XX which passes the sampling point unit at 12:42:01pm could be a good example for low emitter acting as Temporary High Emitter.

For a case from 01.07.2023 - from Table13, the vehicle passing the sampling point unit at 10:12:56 am could be a good example for low emitter acting as high emitter whose emission factor is in the order of 10^{15} #/kg of fuel.



Figure 26 Scatter Plot of point sampling data by EEPS vs Tail pipe test for measurement on 20.10.2022

The Scatter plot depicting the emission Factors calculated from the EEPS Data and the tail pipe measurement using NM3 is shown in Figure 26 and Figure 27, the Points inside the Green line bracket are low emitting vehicles which passed through the sampling point which is obtained by considering the calculated emission factor and data from the tail pipe measurement. The points inside the red line bracket are the clear indication of high emitter vehicle which passed the sampling point on 20.10.2020.


Figure 27 Scatter Plot of point sampling data by EEPS vs Tail pipe test measurement on 01.07.2022

Comparison of two Remote sensing measurement Methods - between EEPS and Nanomet3

Since Nanomet3 is used as a tail measurement Instrument, it can be also used as a remote sensing emission measurement method for which the measurements which were measured by the instrument, which was analyzed, and emission factors were calculated following the same procedure for both measurements done 20.10.2022 and 01.07.2023 and were tabulated as shown in Table 12 and Table 13. A scattered plot or a cluster analysis was carried out for the same number of vehicles on both the days as shown in graph 28 and graph 29. It is observed that the vehicles which were grouped as low emitters from the calculated Emission factors from the data of EEPS which were under the emission limits shown in Graph 26 and Graph 27, which were also under the limit for the emission factors calculated by Nanomet3 data except the fact that the values obtained from NM3 were

slightly lower in magnitude when compared to EEPS, the same pattern was observed in High emitter vehicle group for the measurements from both instruments, EEPS Emission Factor values were higher in magnitude than those from NM3. The trend remains the same for the third group of vehicles, although there was a specific case from 20.10.2022 the vehicle bearing 6AF48XX passing the sampling point at 12.42.01 shows an Emission Factor in the order of 10¹⁴ #/kg of fuel and for NM3 Emission Factor in the order of 10¹⁵ #/kg of fuel as shown in Table 12, which leaves the vehicle in low emitters bracket, Although further inspection is required to know if it was a low emitter, or low emitter acting as temporary high emitter, or an error from the Instruments. It is observed that Emission Factor from Nanomet3 measurements are closer to the Euro limit. Figure 28 depicts the comparison of Emission factors.

PN – Emission factors of both EEPS and Nanomet3 were of slightly higher by few magnitudes than that of Euro limit, and Emission factors calculated from the measurement done by EEPS has slightly higher values than the Emission factors calculated from the measurement done by Nanomet3. This can be explained by the fact that instruments used Nanomet3 measures nonvolatile particles > 10nm used for tail pipe measurement and as a remote sensing instrument but the EEPS as a remote sensing instrument measures particles >5nm including volatile particles and hence wider range in particle size. Secondly the existing emission regulations for example Euro -6, Euro-5b limits, the tests are carried out where the plumes measured are in the range >23nm nonvolatile particles this explains the reason that measurement were above few magnitudes over the Euro limit [18].

For remote sensing method the problem could be a chance of mixing of emissions with other vehicles especially if the vehicles passes at short interval or could be extremely diluted measuring for multiple lanes although these issues are intrinsic drawbacks of roadside measurement but are not restricted, this method can be used for measurement on roads on a large scale to measure large fleet of vehicles to identify the high emitters due to tampering of exhaust after treatment devices and bringing it to their notice for replacement and repair so that vehicle emissions can be reduced.



Figure 28 Scatter Plot of point sampling data by NM3 vs Tail pipe test measurement on 20.10.2022

The Scatter plot depicting the emission Factors calculated from the Nanomet3 Data and the tail pipe measurement using NM3 is shown in Figure 28 and Figure 29, the Points inside the green line bracket are low emitting vehicles which passed through the sampling point which is obtained by considering the calculated emission factor and data from the tail pipe measurement. The points inside the red line bracket are the clear indication of high emitter vehicle which passed the sampling point on 01.07.2023.



Figure 29 Scatter Plot of point sampling data by NM3 vs Tail pipe test measurement on 01.07.2023

Figure 30 and Figure 31 is a graph comparing the calculated Emission Factors of the measurements from EEPS and the calculated Emission Factors from Nanomet3 for each vehicle passage which was recorded on 20.10.2020 and on 01.07.2023.



Figure 28- EF of EEPS v/s Nanomet3 for the measurement on 20.10.2022



Figure 29 - EF for EEPS v/s Nanomet3 for measurement on 01.07.2023

10. Conclusion

This experiment traversed over comparison between a method of compact, cost effective and efficient method of measurement system for identifying high emitters and conventional Tail pipe measurement for the validation of the same. From the camera it was noted that more than 526 vehicles had passed through the sampling point as per the ANPR camera records, out of which for 457 valid sampling point data was obtained from remote emission sensing measurement covering almost over than 85% of the vehicles that had passed through the sampling point at the time of the experiment. Tail pipe measurement was done for 47 selected vehicles. On comparison with remote emission sensing measurement for the same 47 vehicles most of the measurements of remote sensing method measuring vehicle exhaust plumes correlated and had a good agreement with the measures from that of nvPN tail pipe measurement system (PEMS) for the vehicles measured.

Although out of 47vehicles, 39 vehicles had a good correlation in measurements from both measurement method and could be grouped into low emitters and high emitters giving a success rate of 83% for the experiment done on 20.10.2022, the measurement done for remaining 8 cars (17%) it did not correlate with measurement from one method to another making it uncertain if it's a high emitter or low emitter. Could be because of various reasons, for example, low emitter acting as high emitter or Instrumental error in one of the measurement method or Human error, further inspection is required to conclude a certain reason. Out of the valid 47 sampling points, 14% were found to be high emitters, which is a count of 7 vehicles. For the experiment on 01.07.2023 out of 29 vehicles measured, it was possible to get e a data correlation for 79% of 29 vehicles that is, 23 vehicles were grouped into low emitters and high emitters. High emitters were 13%, that is 4 vehicles. By this experiment and methodology, it was feasible to identify high emitters with tampered DPF or malfunction from low emitters from the fleet of Vehicles both on 20.10.2022 and on 01.07.2023 with PN – Emission factor comparison method.

For Type approval [Euro 6, Euro5b] limits [18], for tests the vehicles undergo driving cycles, the limit PN -EF in #/km applies to the average over the cycle. whereas in this experiment, the vehicle exhaust plumes are measured at real road driving conditions and estimate PN-EF in #/kg of fuel which cannot be equal but it gives a clear estimation of how much the emissions are deviated from the Euro Limits, real road driving conditions factors are more complex than the experimental condition factors which affects the performance of this method and there might be a chance of having less number of effective identifications of vehicles as high emitter.

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12. Annexure

Time	Vehicle registration	EF in #/kg of fuel EEPS	EF in #/km	EF gNO/gFuel	EF gCO/gFuel	EF in #/kg of fuel (nanomet3)
12:13:59	8AF 26XX	1.70E+13	8.16E+11	1.50E-02	5.20E-04	2.10E+11
12:14:02	4AX 18XX	5.20E+12	2.50E+11	1.60E-01	1.40E-05	9.10E+11
12:16:42	8AM 38XX	6.60E+09	3.17E+08	1.10E-02	-9.50E-03	3.90E+07
12:18:44	4AF 02XX	2.60E+14	1.25E+13	-3.20E-02	1.10E-03	8.40E+13
12:23:32	8AU 60XX	2.80E+12	1.34E+11	3.50E-03	1.40E-04	2.10E+10
12:23:29	3P8 94XX	1.00E+12	4.80E+10	1.50E-04	1.10E-03	4.50E+11
12:30:45	5S1 42XX	4.00E+15	1.92E+14	5.90E-03	5.30E-04	8.00E+14
12:34:35	3AY 20XX	2.30E+12	1.10E+11	4.30E-03	5.50E-03	2.00E+11
12:42:01	6AF 48XX	7.90E+14	3.79E+13	4.70E-05	7.50E-03	1.90E+13
12:52:41	7AS 44XX	5.70E+12	2.74E+11	-5.50E-04	3.20E-04	8.30E+08
12:52:06	4K7 47XX	1.80E+12	8.64E+10	9.10E-03	-5.40E-03	1.50E+11
12:54:53	8P3 75XX	1.40E+13	6.72E+11	4.50E-03	1.80E-02	2.70E+12
12:57:56	2E9 19XX	3.70E+15	1.78E+14	1.80E-04	-5.20E-03	3.10E+14
12:58:41	5J9 93XX	2.70E+13	1.30E+12	3.70E-02	1.60E-01	2.90E+12
12:58:33	2A1 80XX	9.90E+11	4.75E+10	2.50E-04	1.00E-04	8.60E+10
13:00:37	2SB 27XX	6.10E+16	2.93E+15	3.50E-03	1.60E-01	1.20E+15
13:00:53	8AM 70XX	3.10E+15	1.49E+14	5.90E-03	-5.50E-03	2.70E+14
13:01:34	1TN 38XX	1.00E+12	4.80E+10	1.10E-03	-5.50E-03	1.50E+10
13:02:02	4AI 16XX	1.50E+12	7.20E+10	8.10E-04	1.60E-01	9.20E+11
13:02:48	9AC 26XX	5.50E+10	2.64E+09	4.10E-02	-5.50E-03	1.80E+09
13:08:52	6M2 87XX	3.10E+12	1.49E+11	1.70E-02	9.70E-03	6.20E+10
13:11:35	4AN 27XX	2.60E+11	1.25E+10	9.30E-03	1.60E-01	9.70E+10
13:11:27	6E5 80XX	3.70E+12	1.78E+11	2.50E-02	3.70E-02	4.20E+11
13:11:14	1SX 73XX	4.30E+12	2.06E+11	8.30E-03	6.60E-04	4.90E+08
13:13:09	4AR 93XX	1.30E+12	6.24E+10	2.70E-03	7.90E-05	1.40E+08
13:13:44	3U9 94XX	9.40E+15	4.51E+14	1.10E-02	4.00E-04	9.00E+14
13:14:02	2AV 65XX	2.80E+16	1.34E+15	5.40E-03	8.10E-03	5.50E+14
13:17:01	7AC 27XX	2.70E+12	1.30E+11	5.20E-03	2.20E-05	4.30E+11
13:18:42	1AH 35XX	4.20E+16	2.02E+15	4.30E-04	7.00E-04	3.50E+15
15:26:45	7U4 55XX	2.10E+12	1.01E+11	1.00E-02	-7.60E-06	7.60E+09
15:27:53	2SP 84XX	3.30E+12	1.58E+11	8.20E-03	5.50E-03	6.20E+11
15:30:54	3SH 55XX	2.30E+12	1.10E+11	7.30E-03	-4.90E-03	1.70E+11
15:30:29	8AB 84XX	5.20E+11	2.50E+10	3.30E-04	-5.40E-03	2.60E+07
15:30:58	3SE 06XX	1.70E+12	8.16E+10	1.20E-02	8.70E-04	2.00E+09
15:31:38	3AE 61XX	3.40E+12	1.63E+11	2.30E-03	-2.20E-05	6.80E+10

Table 14 - Table for EF on 20.10.2022

15:32:08	7AP 04XX	2.60E+12	1.25E+11	6.70E-03	1.60E-01	2.80E+10
15:32:31	4AN 24XX	1.30E+15	6.24E+13	1.30E-02	8.80E-03	1.90E+14
15:36:47	1UH 54XX	3.20E+13	1.54E+12	2.80E-03	1.50E-04	5.00E+12
15:38:03	8AM 64XX	2.00E+12	9.60E+10	2.60E-03	9.40E-03	2.20E+11
15:39:12	5AX 05XX	2.10E+12	1.01E+11	5.80E-04	3.30E-03	2.70E+08
15:39:55	7AF 02XX	5.70E+12	2.74E+11	1.00E-02	3.20E-02	1.60E+11
15:40:23	8AM 42XX	1.60E+13	7.68E+11	1.10E-02	1.00E-04	5.20E+11
15:41:09	5SA 39XX	5.00E+10	2.40E+09	5.00E-03	-2.20E-05	4.30E+09
16:00:25	5C7 27XX	4.40E+11	2.11E+10	2.20E-02	7.90E-05	9.30E+09
16:02:07	4ST 08XX	1.60E+11	7.68E+09	1.60E-04	6.10E-04	1.00E+07
16:03:02	6AM 71XX	1.60E+12	7.68E+10	-2.90E-03	2.60E-04	2.90E+11
16:09:31	5AU 47XX	4.30E+12	2.06E+11	7.30E-04	5.50E-03	1.20E+09
14:22:43	4SA50XX	9.40E+12	4.51E+11	2.80E-03	1.20E-04	2.70E+11
14:23:11	8AM97XX	5.70E+12	2.74E+11	9.10E-04	-4.90E-03	1.20E+12
14:37:56	4AL10XX	1.60E+13	7.68E+11	5.20E-03	6.00E-02	5.10E+07
14:43:02	6U147XX	1.70E+12	8.16E+10	-1.30E-03	5.60E-04	1.10E+14
14:44:01	3K037XX	3.10E+12	1.49E+11	-8.00E-04	1.60E-01	2.70E+10
14:45:34	7A793XX	3.00E+12	1.44E+11	4.20E-03	2.50E-03	5.90E+11
14:45:35	7AM29XX	6.60E+09	3.17E+08	8.70E-03	6.60E-03	1.00E+15
14:45:44	3L683XX	1.90E+11	9.12E+09	2.20E-04	6.60E-04	2.60E+11
14:49:01	4AD18XX	1.30E+13	6.24E+11	1.40E-03	1.60E-01	2.40E+13
14:49:57	3AB22XX	1.60E+12	7.68E+10	-4.70E-03	-8.90E-03	1.10E+09
14:50:35	4SF17XX	1.10E+12	5.28E+10	1.90E-04	-4.90E-03	2.00E+11
14:50:47	1TU77XX	7.40E+11	3.55E+10	3.00E-04	-4.90E-03	3.50E+12
14:51:09	7AE45XX	2.80E+11	1.34E+10	2.80E-05	-5.30E-03	4.10E+14
14:52:20	4J358XX	7.70E+11	3.70E+10	5.90E-03	1.90E-02	3.80E+12
14:54:51	3SE76XX	5.70E+12	2.74E+11	1.40E-02	6.90E-04	1.10E+11
14:55:52	MEM35XX	5.80E+11	2.78E+10	1.10E-02	8.00E-03	1.60E+15
14:57:13	8AN50XX	8.60E+11	4.13E+10	-4.20E-02	1.20E-04	3.50E+14
14:58:23	1BA91XX	8.00E+12	3.84E+11	3.60E-03	5.40E-02	1.90E+10
14:58:37	6A403XX	1.70E+12	8.16E+10	1.50E-04	-3.40E-03	1.20E+12
15:00:48	6A015XX	3.20E+11	1.54E+10	5.20E-03	6.10E-04	2.40E+09
15:02:09	1AC17XX	2.80E+11	1.34E+10	1.20E-02	1.60E-03	8.00E+10
15:02:52	8AD59XX	2.30E+12	1.10E+11	2.10E-03	1.10E-02	1.30E+11
15:03:14	6AR94XX	7.40E+12	3.55E+11	9.00E-03	1.60E-01	5.40E+11
15:03:24	2SL07XX	2.70E+12	1.30E+11	4.50E-03	1.30E-01	6.40E+08
15:04:45	9S114XX	2.60E+11	1.25E+10	2.60E-04	2.10E-05	1.90E+08
15:05:56	4ST14XX	3.00E+12	1.44E+11	5.00E-03	6.60E-04	1.20E+15
15:11:49	5L646XX	9.20E+12	4.42E+11	2.20E-02	-4.80E-03	7.10E+14
15:12:29	2S827XX	1.80E+12	8.64E+10	1.60E-04	1.20E-02	5.60E+11
15:12:59	7AT84XX	7.20E+11	3.46E+10	-2.90E-03	5.00E-05	4.50E+15
15:13:35	3AK82XX	9.80E+11	4.70E+10	7.30E-04	5.70E-04	9.90E+09
15:14:31	3SV18XX	8.70E+11	4.18E+10	2.80E-03	-2.30E-06	8.10E+11

15:15:41	3L809XX	2.50E+11	1.20E+10	9.10E-04	1.10E-04	2.20E+11
15:16:08	5SD71XX	2.90E+12	1.39E+11	5.20E-03	-5.00E-03	3.40E+07
15:16:16	3SF57XX	3.30E+12	1.58E+11	-1.30E-03	1.00E-05	2.60E+09
15:16:45	8AI76XX	5.20E+11	2.50E+10	-8.00E-04	3.70E-02	8.80E+10
15:19:14	4AD21XX	8.30E+09	3.98E+08	4.20E-03	1.10E-02	3.70E+10
15:19:57	5SP8XX	1.30E+11	6.24E+09	8.70E-03	3.10E-02	2.50E+14
15:22:43	5AZ77XX	2.70E+11	1.30E+10	2.20E-04	5.80E-04	6.50E+12
15:23:08	7A673XX	6.40E+12	3.07E+11	1.40E-03	3.10E-02	2.80E+11
15:23:28	8AK76XX	1.80E+12	8.64E+10	-4.70E-03	-4.90E-03	3.50E+08
15:24:07	8AZ29XX	2.10E+12	1.01E+11	1.90E-04	5.80E-04	2.10E+11
15:27:02	6AP83XX	1.30E+13	6.24E+11	3.00E-04	8.70E-04	6.70E+11
15:27:24	5AM50XX	1.00E+12	4.80E+10	2.80E-05	1.50E-02	5.60E+09
15:27:53	2AR31XX	4.00E+11	1.92E+10	5.90E-03	5.80E-04	1.20E+10
15:29:39	8AM65XX	3.10E+12	1.49E+11	6.10E-03	1.20E-03	1.40E+07
15:29:48	3AV91XX	1.80E+12	8.64E+10	1.10E-02	3.20E-02	3.80E+11
15:29:54	7P673XX	1.50E+11	7.20E+09	1.60E-04	5.90E-04	1.60E+09
15:30:26	7AA25XX	5.00E+13	2.40E+12	1.00E-02	1.10E-03	2.30E+11
15:31:45	4SZ04XX	1.90E+11	9.12E+09	2.00E-04	5.00E-04	1.00E+12
15:31:57	7AH04XX	2.70E+12	1.30E+11	9.00E-04	-5.50E-03	4.30E+07
15:32:31	8AX30XX	7.70E+11	3.70E+10	5.20E-03	5.30E-04	9.30E+13
15:32:48	4ST01XX	1.70E+10	8.16E+08	-2.10E-02	6.70E-04	2.30E+10
15:33:33	8AC84XX	9.20E+12	4.42E+11	-9.10E-04	3.70E-02	5.00E+11
15:34:51	4SP44XX	1.50E+10	7.20E+08	4.00E-03	3.10E-02	8.70E+14
15:39:01	4SR40XX	1.70E+12	8.16E+10	8.90E-03	8.80E-03	2.20E+11
15:42:05	4A824XX	1.30E+11	6.24E+09	2.20E-04	-5.50E-03	2.10E+13
15:42:39	EL382XX	8.70E+11	4.18E+10	1.40E-03	-3.80E-03	9.10E+08
15:44:47	3AY12XX	2.10E+12	1.01E+11	-7.40E-03	-5.50E-03	1.70E+11
15:45:38	7M247XX	2.00E+12	9.60E+10	1.90E-04	1.70E-03	2.90E+12
15:47:47	1SE38XX	3.10E+11	1.49E+10	3.00E-04	7.90E-05	3.50E+14
15:48:07	2AI23XX	3.10E+12	1.49E+11	3.40E-05	5.70E-04	3.20E+12
15:48:57	7AA28XX	1.70E+11	8.16E+09	5.90E-03	-5.40E-03	9.50E+10
15:49:11	7AS08XX	5.30E+12	2.54E+11	7.10E-03	3.70E-02	1.40E+15
15:52:02	6AT90XX	2.10E+12	1.01E+11	5.20E-03	-5.40E-03	3.00E+14
15:54:11	5AY84XX	2.80E+12	1.34E+11	4.30E-04	2.10E-05	1.60E+10
15:54:41	4SV12XX	6.10E+12	2.93E+11	1.00E-02	6.80E-04	1.00E+12
8:52:34	2AZ87XX	9.10E+11	4.37E+10	8.20E-03	-5.50E-03	2.00E+09
8:52:52	7P673XX	5.20E+08	2.50E+07	7.30E-03	-5.40E-03	6.80E+10
8:53:13	4SC09XX	1.80E+12	8.64E+10	3.30E-04	-5.40E-03	1.10E+11
8:53:42	4SM74XX	2.70E+13	1.30E+12	1.20E-02	1.80E-02	4.60E+11
8:54:25	4AT74XX	6.40E+11	3.07E+10	2.30E-03	9.90E-05	5.40E+08
8:55:56	5U077XX	2.30E+12	1.10E+11	6.70E-03	-5.50E-03	1.60E+08
8:56:21	6AK79XX	2.00E+12	9.60E+10	1.30E-02	-4.90E-03	9.90E+14
8:57:59	8AX29XX	5.10E+12	2.45E+11	2.80E-03	-2.20E-05	6.00E+14

8:58:13	1AX28XX	8.70E+11	4.18E+10	2.60E-03	9.00E-04	4.80E+11
8:59:49	5SJ77XX	3.00E+12	1.44E+11	5.80E-04	-5.00E-04	3.80E+15
9:00:32	IUL96XX	2.00E+12	9.60E+10	1.00E-02	2.00E-03	8.40E+09
9:01:04	6AN15XX	5.90E+10	2.83E+09	1.50E-01	4.00E-04	6.80E+11
9:01:16	7AM29XX	1.80E+11	8.64E+09	1.50E-01	1.00E-03	1.90E+11
9:03:00	1SZ33XX	2.60E+12	1.25E+11	2.30E-03	4.20E-05	2.90E+07
9:03:10	4SU24XX	1.70E+12	8.16E+10	4.10E-02	-3.20E-05	2.20E+09
9:05:29	6AT85XX	2.70E+12	1.30E+11	5.60E-03	-5.50E-03	7.40E+10
9:09:41	7AU69XX	2.70E+11	1.30E+10	8.90E-03	9.90E-05	3.10E+10
9:10:21	1AU88XX	3.70E+12	1.78E+11	3.20E-03	-5.50E-03	2.10E+14
9:11:06	8U433XX	3.10E+11	1.49E+10	4.80E-03	4.00E-04	5.50E+12
9:12:24	4AI57XX	4.30E+12	2.06E+11	9.00E-03	5.30E-04	2.40E+11
9:13:22	8AR75XX	2.60E+12	1.25E+11	9.60E-03	-5.50E-03	3.00E+08
9:15:53	4T103XX	2.30E+12	1.10E+11	5.60E-06	1.30E-01	1.80E+11
9:16:09	8AA38XX	5.80E+12	2.78E+11	4.60E-03	3.70E-02	5.70E+11
9:16:20	5AB51XX	1.60E+12	7.68E+10	8.90E-03	5.50E-02	4.80E+09
9:19:45	3K984XX	2.60E+12	1.25E+11	2.80E-02	-5.50E-03	1.00E+10
9:20:29	5AS93XX	3.10E+12	1.49E+11	8.80E-03	-5.40E-03	1.10E+07
9:21:01	6U522XX	3.20E+08	1.54E+07	5.60E-03	3.70E-02	3.20E+11
9:22:09	7AA59XX	6.10E+12	2.93E+11	3.20E-03	1.50E-01	1.40E+09
9:22:22	IUH08XX	3.30E+10	1.58E+09	7.90E-03	3.10E-02	1.90E+11
9:23:19	8AL40XX	3.40E+12	1.63E+11	8.20E-03	-3.20E-05	8.20E+11
9:24:27	7P673XX	1.10E+13	5.28E+11	3.10E-02	7.10E-04	3.50E+07
9:25:11	2SL07XX	5.10E+10	2.45E+09	7.50E-03	1.00E-03	7.60E+13
9:26:49	3U297XX	3.10E+11	1.49E+10	2.50E-04	1.60E-01	1.80E+10
9:27:35	6AP64XX	7.20E+12	3.46E+11	1.60E-02	-5.50E-03	4.10E+11
9:29:54	7A631XX	3.30E+12	1.58E+11	7.90E-04	-1.00E-05	7.20E+14
9:32:31	5A217XX	5.80E+11	2.78E+10	6.40E-03	-4.90E-03	1.80E+11
9:36:16	5AD04XX	2.90E+12	1.39E+11	2.20E-03	6.00E-02	1.70E+13
9:37:05	2ST89XX	3.00E+12	1.44E+11	3.60E-03	-5.40E-03	7.50E+08
9:37:31	1AF60XX	1.00E+12	4.80E+10	3.90E-03	-6.00E-03	1.40E+11
9:40:36	6AN96XX	8.70E+11	4.18E+10	8.60E-03	-5.50E-03	2.40E+12
9:41:08	3AU63XX	2.80E+12	1.34E+11	1.10E-03	5.00E-05	2.80E+14
9:41:15	2L081XX	7.90E+11	3.79E+10	8.70E-04	6.60E-04	2.60E+12
9:41:27	4SU27XX	4.80E+12	2.30E+11	1.80E-03	5.40E-02	7.80E+10
9:43:58	4U106XX	6.00E+12	2.88E+11	8.70E-03	-5.40E-03	1.10E+15
9:47:14	8AJ28XX	2.80E+12	1.34E+11	3.20E-03	5.80E-05	2.40E+14
9:50:33	8AE04XX	2.80E+11	1.34E+10	6.70E-03	6.50E-04	1.30E+10
9:51:05	4SJ75XX	1.00E+12	4.80E+10	2.40E-03	-5.40E-03	8.30E+11
9:51:33	4S212XX	1.10E+12	5.28E+10	4.30E-03	5.90E-04	1.70E+09
9:51:58	FMO78XX	1.20E+13	5.76E+11	6.30E-03	-5.50E-03	5.60E+10
9:52:40	PHM92XX	1.30E+13	6.24E+11	6.50E-03	-5.30E-03	8.70E+10
9:52:53	6AA35XX	1.10E+12	5.28E+10	8.50E-03	-4.30E-03	3.80E+11

9:53:50	2SB96XX	1.00E+12	4.80E+10	9.30E-04	1.30E-02	4.40E+08
9:55:14	7U861XX	5.70E+12	2.74E+11	2.40E-03	-5.50E-03	1.30E+08
9:55:33	5AV68XX	6.10E+12	2.93E+11	4.00E-03	1.50E-04	8.10E+14
9:56:08	4SZ18XX	1.60E+11	7.68E+09	1.30E-02	6.70E-04	4.90E+14
9:56:23	2TE94XX	1.30E+11	6.24E+09	8.90E-03	-5.00E-03	3.90E+11
9:56:35	4U494XX	1.10E+13	5.28E+11	1.20E-02	-5.50E-03	3.10E+15
9:56:37	4Q494XX	2.80E+11	1.34E+10	8.30E-03	5.80E-05	6.80E+09
9:56:41	7AU83XX	8.70E+11	4.18E+10	6.30E-03	5.60E-04	5.60E+11
9:57:39	4AM61XX	4.40E+11	2.11E+10	8.10E-03	-5.40E-03	1.50E+11
9:58:15	3SC84XX	1.00E+12	4.80E+10	3.80E-03	5.70E-04	2.30E+07
9:58:49	3AB22XX	3.00E+11	1.44E+10	1.00E-02	8.80E-03	1.80E+09
10:00:07	3C663XX	3.00E+12	1.44E+11	9.90E-03	-5.00E-04	6.10E+10
10:00:40	5AE79XX	2.80E+12	1.34E+11	4.90E-03	1.60E-01	2.60E+10
10:00:48	6AI43XX	2.90E+12	1.39E+11	3.30E-04	2.50E-03	1.70E+14
10:01:03	5AH85XX	3.30E+12	1.58E+11	8.80E-03	-5.20E-05	4.50E+12
10:01:22	4SC35XX	1.10E+12	5.28E+10	7.70E-03	-5.60E-03	2.00E+11
10:01:31	7AC30XX	8.60E+11	4.13E+10	1.40E-02	-5.50E-03	2.40E+08
10:03:30	9U930XX	1.00E+12	4.80E+10	8.90E-03	5.70E-04	1.50E+11
10:04:30	2A730XX	2.10E+12	1.01E+11	8.80E-03	1.10E-04	4.60E+11
10:04:45	8AI14XX	1.60E+11	7.68E+09	9.00E-03	6.10E-04	3.90E+09
10:05:19	5AC35XX	3.10E+12	1.49E+11	3.20E-03	1.20E-03	8.40E+09
10:05:37	5AF02XX	1.00E+12	4.80E+10	4.80E-03	6.60E-04	9.40E+06
10:05:50	AKR86XX	5.70E+10	2.74E+09	2.20E-03	-5.40E-03	2.60E+11
10:06:34	5SV53XX	3.30E+12	1.58E+11	5.10E-02	5.40E-04	1.10E+09
10:07:02	1AY46XX	2.80E+12	1.34E+11	5.50E-03	6.00E-03	2.50E+11
10:07:36	2AJ14XX	2.50E+11	1.20E+10	8.90E-03	-5.40E-03	1.10E+12
10:07:47	1P2020XX	1.70E+12	8.16E+10	3.80E-03	6.50E-06	4.60E+07
10:07:55	8U699XX	4.00E+12	1.92E+11	2.60E-03	3.10E-02	9.90E+13
10:08:08	3SE72XX	1.30E+11	6.24E+09	6.90E-03	5.60E-04	2.40E+10
10:09:19	3SB77XX	5.50E+10	2.64E+09	5.40E-05	3.70E-02	5.30E+11
10:10:20	6L076XX	8.70E+11	4.18E+10	4.60E-03	-5.40E-03	9.30E+14
10:13:11	2K939XX	4.00E+11	1.92E+10	8.80E-03	-4.60E-03	2.30E+11
10:13:19	7AL32XX	7.40E+11	3.55E+10	4.00E-03	5.80E-04	2.20E+13
10:13:26	3K306XX	4.30E+12	2.06E+11	1.30E-02	8.10E-03	9.70E+08
10:13:44	3SN89XX	3.50E+10	1.68E+09	8.90E-03	1.30E-01	1.80E+11
10:14:00	EL71XX	3.00E+12	1.44E+11	1.20E-02	-5.50E-03	3.10E+12
10:14:06	7AX66XX	6.70E+10	3.22E+09	8.30E-03	1.50E-02	3.70E+14
10:14:13	7AV45XX	1.60E+12	7.68E+10	6.30E-03	-5.40E-03	3.40E+12
10:14:20	2C877XX	7.20E+11	3.46E+10	8.10E-03	-5.00E-03	1.00E+11
10:14:42	9AL10XX	1.20E+12	5.76E+10	3.80E-03	1.10E-02	1.40E+15
10:14:50	6AN15XX	7.40E+12	3.55E+11	1.00E-02	-1.80E-03	3.20E+14
10:16:04	7AP04XX	1.30E+12	6.24E+10	9.90E-03	9.20E-03	1.70E+10
10:16:34	6AC66XX	2.80E+12	1.34E+11	4.90E-03	1.20E-04	1.10E+12

10:17:25	4AB93XX	2.80E+12	1.34E+11	3.30E-04	1.30E-02	2.20E+09
10:19:06	3B290XX	2.30E+12	1.10E+11	8.80E-03	1.30E-04	7.20E+10
10:20:05	7AH86XX	1.10E+10	5.28E+08	7.70E-03	4.90E-04	1.10E+11
10:21:04	6C779XX	3.00E+12	1.44E+11	1.40E-02	-5.10E-03	4.90E+11
10:21:30	5SI66XX	2.80E+12	1.34E+11	8.90E-03	2.50E-05	5.70E+08
10:21:36	IUH86XX	1.90E+11	9.12E+09	8.80E-03	2.10E-05	1.70E+08
10:22:09	8A744XX	2.40E+11	1.15E+10	9.00E-03	9.20E-03	1.10E+15
10:22:51	PZI26XX	6.80E+12	3.26E+11	3.20E-03	-5.00E-03	6.40E+14
10:22:59	1AN82XX	3.60E+10	1.73E+09	2.90E-03	3.80E-03	5.10E+11
10:23:19	5SB01XX	1.90E+11	9.12E+09	2.40E-03	-5.40E-03	4.10E+15
10:24:18	5AY39XX	1.20E+12	5.76E+10	8.90E-03	3.70E-02	8.90E+09
10:25:13	6AX86XX	9.90E+11	4.75E+10	1.20E-03	1.30E-01	7.30E+11
10:25:21	9AB15XX	1.60E+12	7.68E+10	8.90E-03	6.60E-03	2.00E+11
10:25:29	7AY86XX	2.70E+12	1.30E+11	8.20E-03	1.50E-01	3.00E+07
10:26:11	9AI06XX	4.40E+11	2.11E+10	3.80E-03	1.50E-01	2.30E+09
10:26:18	9U678XX	5.40E+10	2.59E+09	3.00E-02	6.50E-06	7.90E+10
10:26:54	4SA39XX	2.30E+12	1.10E+11	1.00E-02	9.40E-03	3.30E+10
10:27:47	2SA09XX	7.40E+12	3.55E+11	5.00E-03	-5.50E-03	2.20E+14
10:28:11	6B689XX	5.10E+12	2.45E+11	2.00E-04	2.10E-05	5.80E+12
10:28:38	6H176XX	4.40E+11	2.11E+10	8.80E-03	-7.60E-06	2.50E+11
10:31:32	AB1050XX	3.00E+11	1.44E+10	7.70E-03	5.80E-04	3.20E+08
10:33:24	5SK72XX	1.60E+12	7.68E+10	1.70E-02	5.00E-04	1.90E+11
10:33:37	7J172XX	4.00E+12	1.92E+11	8.90E-03	1.30E-04	6.00E+11
10:33:53	6J109XX	2.80E+12	1.34E+11	8.80E-03	5.90E-04	5.10E+09
10:36:40	3K546XX	1.90E+11	9.12E+09	9.00E-03	6.90E-04	1.10E+10
10:37:43	5AR83XX	1.50E+11	7.20E+09	3.20E-03	-5.50E-03	1.20E+07
10:44:35	4Z684XX	1.70E+12	8.16E+10	2.00E-03	6.50E-04	3.40E+11
10:47:03	6AD63XX	3.70E+11	1.78E+10	3.90E-03	8.10E-04	1.40E+09
10:48:12	4SE25XX	2.30E+12	1.10E+11	8.60E-03	-4.90E-03	2.10E+11
10:49:40	1SV80XX	1.00E+12	4.80E+10	1.10E-03	8.80E-03	9.10E+11
10:49:59	2BR81XX	1.60E+12	7.68E+10	8.70E-04	-5.50E-03	3.90E+07
10:50:12	3AK65XX	1.30E+12	6.24E+10	1.80E-03	1.80E-02	8.40E+13
10:51:57	4AA06XX	8.60E+11	4.13E+10	8.70E-03	5.40E-03	2.00E+10
10:54:21	1AC37XX	3.10E+12	1.49E+11	3.20E-03	6.70E-04	4.50E+11
10:54:34	8AA68XX	1.60E+12	7.68E+10	6.70E-03	5.60E-04	7.90E+14
10:55:16	9AD14XX	1.50E+13	7.20E+11	2.40E-03	-5.30E-03	2.00E+11
10:57:40	4AX28XX	2.70E+12	1.30E+11	4.30E-03	-4.40E-03	1.90E+13
10:58:24	7A528XX	1.60E+12	7.68E+10	6.30E-03	-4.90E-03	8.20E+08
10:59:01	8AY63XX	5.10E+12	2.45E+11	6.50E-03	5.50E-04	1.50E+11
10:59:13	6AL37XX	3.60E+10	1.73E+09	8.50E-03	4.20E-03	2.60E+12
11:00:39	4U240XX	3.00E+12	1.44E+11	9.30E-04	1.10E-02	3.10E+14
11:00:51	6AN15XX	9.80E+11	4.70E+10	1.70E-02	1.50E-02	2.90E+12
11:01:29	9AI17XX	2.70E+12	1.30E+11	1.60E-01	4.20E-03	8.50E+10

11:05:09	6E813XX	8.70E+11	4.18E+10	1.30E-02	2.60E-04	1.20E+15
11:07:14	6A015XX	5.40E+09	2.59E+08	-3.00E-02	9.40E-03	2.70E+14
11:10:29	4AP71XX	5.70E+12	2.74E+11	5.30E-03	-5.40E-03	1.50E+10
11:14:04	5AF42XX	9.40E+09	4.51E+08	2.00E-03	1.60E-01	9.10E+11
11:14:47	4SY90XX	8.00E+12	3.84E+11	7.70E-03	8.10E-04	1.80E+09
11:17:24	5SX21XX	2.00E+12	9.60E+10	6.10E-03	4.20E-05	6.10E+10
11:19:55	7C840XX	2.00E+12	9.60E+10	1.90E-03	7.10E-03	9.60E+10
11:21:01	7AD00XX	1.70E+12	8.16E+10	1.30E-03	7.10E-03	4.10E+11
11:23:39	3AN06XX	2.80E+12	1.34E+11	1.10E-02	1.30E-02	4.80E+08
11:24:28	8S155XX	1.80E+12	8.64E+10	6.30E-03	-5.50E-03	1.40E+08
11:25:55	3PSIAJXX	1.70E+12	8.16E+10	2.00E-03	-4.80E-03	8.90E+14
11:27:08	5AU44XX	1.20E+12	5.76E+10	3.90E-02	-5.00E-03	5.40E+14
11:27:41	PZI26XX	5.80E+11	2.78E+10	2.10E-03	6.30E-04	4.30E+11
11:27:52	4AA50XX	2.80E+12	1.34E+11	5.30E-03	5.40E-04	3.40E+15
11:28:21	IUJ63XX	9.20E+12	4.42E+11	7.70E-03	-5.40E-03	7.50E+09
11:28:54	8AX24XX	3.10E+11	1.49E+10	2.90E-03	5.50E-04	6.20E+11
11:31:09	3SC16XX	3.10E+12	1.49E+11	2.60E-03	3.70E-02	1.70E+11
11:31:32	5SK45XX	1.00E+12	4.80E+10	4.20E-02	-6.00E-03	2.60E+07
11:32:32	7P673XX	2.10E+12	1.01E+11	1.80E-02	1.90E-02	2.00E+09
11:34:19	AHR44XX	5.30E+12	2.54E+11	1.10E-02	-5.50E-03	6.70E+10
11:35:33	KLJ14XX	2.60E+12	1.25E+11	2.70E-02	-5.40E-03	2.80E+10
11:36:32	5P79XX	3.60E+11	1.73E+10	1.00E-02	-4.80E-03	1.90E+14
11:38:03	4SF57XX	6.40E+12	3.07E+11	4.50E-03	-5.40E-03	4.90E+12
11:38:12	6J120XX	1.00E+12	4.80E+10	1.30E-02	5.70E-04	2.10E+11
11:38:38	5AM85XX	1.60E+13	7.68E+11	7.20E-03	-4.60E-03	2.70E+08
11:38:44	1SL64XX	9.10E+11	4.37E+10	7.00E-03	9.00E-04	1.60E+11
11:38:54	5SC28XX	4.80E+12	2.30E+11	2.20E-03	-5.40E-03	5.10E+11
11:39:56	2J677XX	1.30E+12	6.24E+10	1.20E-02	3.30E-03	4.30E+09
11:40:59	7A647XX	1.60E+12	7.68E+10	1.00E-02	1.10E-03	9.20E+09
11:41:59	8C803XX	6.40E+12	3.07E+11	9.10E-03	5.70E-04	1.00E+07
11:42:27	6SA62XX	1.40E+11	6.72E+09	2.10E-03	-4.80E-03	2.90E+11
11:44:27	EL344XX	6.40E+12	3.07E+11	1.40E-02	1.60E-01	1.20E+09
11:44:54	6AJ88XX	2.70E+13	1.30E+12	4.20E-03	-1.20E-05	1.40E+11
11:45:17	3H556XX	1.30E+12	6.24E+10	8.50E-03	-5.40E-03	6.30E+11
11:45:59	AKU10XX	3.70E+11	1.78E+10	1.50E-02	1.20E-04	2.70E+07
11:46:47	8AZ29XX	2.60E+11	1.25E+10	4.60E-03	8.10E-04	5.80E+13
11:47:24	1AS98XX	9.90E+11	4.75E+10	4.40E-03	1.10E-04	1.40E+10
11:47:30	1AH65XX	8.70E+11	4.18E+10	2.40E-03	6.70E-04	3.10E+11
11:47:44	6P831XX	1.50E+12	7.20E+10	1.20E-02	1.10E-04	5.40E+14
11:47:49	5SL19XX	1.70E+12	8.16E+10	1.30E-02	6.30E-04	1.40E+11
11:48:01	4SM47XX	9.80E+11	4.70E+10	6.80E-03	1.60E-01	1.30E+13
11:49:41	7AT63XX	1.50E+12	7.20E+10	2.40E-02	5.80E-05	5.70E+08
11:50:06	8AX29XX	1.60E+09	7.68E+07	2.00E-03	1.30E-02	1.00E+11

11:50:16	9AI31XX	1.40E+10	6.72E+08	-1.10E-03	-5.20E-03	1.80E+12
11:50:34	2AA84XX	9.40E+12	4.51E+11	2.50E-03	4.20E-05	2.10E+14
11:51:08	8AF13XX	6.50E+11	3.12E+10	4.60E-03	2.50E-05	2.00E+12
11:51:46	2BD24XX	5.80E+12	2.78E+11	2.70E-03	2.50E-03	5.90E+10
11:53:33	5AX13XX	2.60E+11	1.25E+10	7.00E-03	-5.10E-03	8.50E+14
11:54:04	8AY64XX	9.20E+12	4.42E+11	4.60E-04	1.60E-04	1.90E+14
11:54:35	2SF63XX	3.60E+11	1.73E+10	1.00E-03	-5.40E-03	1.00E+10
11:54:55	8AH08XX	9.80E+11	4.70E+10	6.00E-03	-5.40E-03	6.30E+11
11:55:16	8AL50XX	1.80E+11	8.64E+09	1.10E-02	-4.00E-03	1.30E+09
11:55:48	2AE70XX	2.30E+12	1.10E+11	2.00E-03	-3.40E-03	4.20E+10
11:56:02	2AE70XX	3.20E+11	1.54E+10	3.20E-03	-5.40E-03	6.60E+10
11:56:04	8AJ10XX	3.70E+11	1.78E+10	-2.90E-03	3.70E-02	2.90E+11
11:57:30	8AI99XX	1.00E+12	4.80E+10	2.00E-03	9.40E-03	3.30E+08
11:57:58	9AH88XX	1.30E+13	6.24E+11	2.10E-03	5.70E-04	9.90E+07
11:58:25	1AC59XX	4.20E+11	2.02E+10	1.80E-03	1.30E-01	6.20E+14
11:58:57	8U468XX	1.80E+12	8.64E+10	7.70E-03	9.40E-03	3.70E+14
11:59:14	9A583XX	9.80E+11	4.70E+10	1.60E-02	3.30E-03	3.00E+11
11:59:46	9AA83XX	2.80E+12	1.34E+11	1.30E-02	1.50E-03	2.40E+15
12:00:06	9S561XX	3.10E+12	1.49E+11	-4.10E-02	1.20E-02	5.20E+09
12:00:15	8AX74XX	2.70E+12	1.30E+11	5.40E-03	5.40E-04	4.30E+11
12:00:28	ELI53XX	5.70E+12	2.74E+11	2.00E-03	-5.50E-03	1.20E+11
12:00:37	9A583XX	1.80E+12	8.64E+10	7.00E-03	6.90E-04	1.80E+07
12:00:45	9A583XX	1.60E+12	7.68E+10	1.30E-02	-5.00E-03	1.40E+09
12:01:18	7AE99XX	6.80E+12	3.26E+11	3.90E-03	4.90E-04	4.60E+10
12:01:54	1SI13XX	1.50E+11	7.20E+09	1.10E-02	-4.00E-03	1.90E+10
12:02:49	8AV94XX	6.40E+12	3.07E+11	6.30E-03	5.40E-04	1.30E+14
12:03:04	7S997XX	9.10E+11	4.37E+10	2.10E-03	1.40E-05	3.40E+12
12:03:55	3SU18XX	5.80E+11	2.78E+10	6.80E-03	5.40E-03	1.50E+11
12:04:02	8AN91XX	5.30E+12	2.54E+11	2.40E-02	-4.90E-03	1.90E+08
12:05:05	7AI00XX	1.70E+12	8.16E+10	2.00E-03	8.00E-03	1.10E+11
12:05:42	6A271XX	2.80E+12	1.34E+11	-1.10E-03	4.90E-04	3.50E+11
12:05:46	5AZ15XX	4.00E+12	1.92E+11	2.50E-03	-1.80E-03	3.00E+09
12:05:50	1AC35XX	9.10E+11	4.37E+10	4.60E-03	8.50E-03	6.30E+09
12:06:08	4S629XX	5.10E+12	2.45E+11	2.70E-03	-4.90E-03	7.10E+08
12:07:32	4AJ07XX	5.30E+11	2.54E+10	7.00E-03	3.30E-03	2.00E+11
12:07:52	2A287XX	8.60E+11	4.13E+10	4.60E-04	5.20E-04	8.40E+08
12:07:59	EL320XX	2.70E+12	1.30E+11	1.00E-03	3.20E-04	1.90E+11
12:08:26	9AF96XX	2.50E+11	1.20E+10	6.00E-03	-5.50E-03	8.10E+11
12:09:37	8P690XX	4.10E+09	1.97E+08	1.10E-02	2.20E-05	3.50E+07
12:11:59	8AF26XX	7.90E+11	3.79E+10	2.00E-03	1.40E-04	7.50E+13
12:12:16	DW6SSXX	2.70E+12	1.30E+11	3.20E-03	-4.30E-03	1.80E+10
12:13:02	4AX18XX	9.40E+12	4.51E+11	-2.90E-03	1.80E-02	4.00E+11
12:15:42	8AM38XX	2.30E+12	1.10E+11	2.00E-03	-5.00E-03	7.10E+14

12:16:44	4AF02XX	7.20E+11	3.46E+10	2.10E-03	9.50E-04	1.80E+11
12:17:37	9AF37XX	1.40E+10	6.72E+08	1.80E-03	1.60E-04	1.70E+13
12:18:11	6AR23XX	5.00E+13	2.40E+12	7.70E-03	-5.50E-03	7.40E+08
12:19:39	2SH78XX	1.10E+13	5.28E+11	7.90E-03	1.10E-04	1.40E+11
12:20:49	2SL79XX	5.20E+10	2.50E+09	1.30E-02	-5.50E-03	2.40E+12
12:21:32	8AU60XX	2.80E+12	1.34E+11	2.00E-03	1.50E-01	2.80E+14
12:22:29	3P894XX	1.80E+12	8.64E+10	1.20E-02	1.40E-04	2.60E+12
12:23:01	IUH08XX	3.10E+12	1.49E+11	2.00E-03	3.70E-02	7.70E+10
12:23:52	7P673XX	3.70E+12	1.78E+11	2.70E-03	5.70E-04	1.10E+15
12:25:25	7AN90XX	1.30E+12	6.24E+10	7.00E-03	6.60E-04	2.40E+14
12:26:56	2A990XX	9.20E+12	4.42E+11	-1.90E-02	5.60E-04	1.30E+10
12:28:45	5SI42XX	6.00E+12	2.88E+11	9.00E-04	1.80E-02	8.20E+11
12:30:46	6P983XX	5.00E+10	2.40E+09	5.90E-03	1.60E-01	1.60E+09
12:31:03	7AA94XX	2.80E+12	1.34E+11	1.10E-02	1.10E-04	5.50E+10
12:31:14	5SI07XX	1.10E+12	5.28E+10	2.00E-03	3.30E-03	8.60E+10
12:33:35	3AY20XX	1.20E+13	5.76E+11	3.20E-03	7.50E-03	3.70E+11
12:38:21	L666XX	3.00E+12	1.44E+11	-5.60E-03	-5.50E-03	4.30E+08
12:38:40	9S242XX	5.80E+10	2.78E+09	2.00E-03	-5.40E-03	1.30E+08
12:40:04	6H885XX	2.40E+09	1.15E+08	2.10E-03	-5.50E-03	8.00E+14
12:40:37	2AI65XX	2.60E+12	1.25E+11	1.80E-03	1.80E-02	4.80E+14
12:41:01	6AF48XX	5.70E+12	2.74E+11	7.70E-03	6.80E-04	3.80E+11
12:44:04	5SD09XX	3.50E+10	1.68E+09	8.90E-03	-9.50E-03	3.10E+15
12:45:02	9AD13XX	1.10E+09	5.28E+07	7.00E-03	-2.30E-06	6.80E+09
12:45:25	2AL84XX	7.40E+12	3.55E+11	2.20E-03	1.40E-05	5.50E+11
12:46:35	4L357XX	2.60E+11	1.25E+10	1.20E-02	5.70E-04	1.50E+11
12:48:25	5L086XX	4.40E+11	2.11E+10	1.00E-02	6.50E-04	2.30E+07
12:50:41	7AS44XX	2.80E+11	1.34E+10	9.10E-03	-4.50E-03	1.80E+09
12:52:06	4K747XX	2.00E+12	9.60E+10	2.10E-03	-1.20E-05	6.00E+10
12:52:53	8P375XX	1.00E+12	4.80E+10	1.40E-02	8.50E-03	2.50E+10
12:53:08	8P375XX	7.40E+12	3.55E+11	4.20E-03	1.50E-03	1.70E+14
12:53:36	9AA88XX	9.10E+09	4.37E+08	8.50E-03	-4.60E-03	4.40E+12
12:55:40	KLN58XX	2.30E+12	1.10E+11	1.50E-02	3.70E-02	1.90E+11
12:55:56	2E919XX	1.80E+12	8.64E+10	4.60E-03	6.00E-02	2.40E+08
12:56:41	5J993XX	7.70E+11	3.70E+10	4.40E-03	-5.50E-03	1.40E+11
12:57:33	2AI80XX	1.70E+12	8.16E+10	2.40E-03	1.20E-05	4.60E+11
12:59:13	9AD11XX	3.40E+12	1.63E+11	1.20E-02	-5.20E-05	3.90E+09
12:59:37	2SB27XX	3.10E+11	1.49E+10	1.50E-01	1.60E-01	8.30E+09
13:00:53	8AM70XX	5.00E+13	2.40E+12	1.50E-01	-5.40E-03	9.30E+08
13:01:34	1TN38XX	4.20E+11	2.02E+10	4.10E-03	-4.90E-03	2.60E+11
13:01:57	1TN38XX	8.70E+11	4.18E+10	4.30E-02	-5.50E-03	1.10E+09
13:02:02	4AI16XX	2.60E+12	1.25E+11	7.40E-03	1.00E-05	1.60E+11
13:02:26	4AI16XX	1.00E+12	4.80E+10	1.10E-02	1.70E-03	6.90E+11
13:02:31	9U559XX	3.30E+12	1.58E+11	5.00E-03	-5.60E-03	2.90E+07

13:02:43	5SU57XX	1.70E+12	8.16E+10	6.60E-03	-4.90E-03	6.40E+13
13:02:48	9AC26XX	1.30E+10	6.24E+08	1.10E-02	-4.10E-03	1.50E+10
13:09:20	4AN27XX	3.50E+10	1.68E+09	1.10E-02	7.10E-04	3.40E+11
13:10:27	6E580XX	3.00E+11	1.44E+10	1.80E-03	5.40E-04	6.00E+14
13:11:14	1SX73XX	2.80E+12	1.34E+11	6.40E-03	5.40E-04	1.50E+11
13:12:09	4AR93XX	2.70E+12	1.30E+11	1.10E-02	3.10E-02	8.96E+09
13:12:44	3U994XX	2.60E+12	1.25E+11	2.90E-02	1.10E-04	5.60E+11
13:14:02	2AV65XX	9.90E+11	4.75E+10	1.10E-02	1.60E-01	1.12E+09
13:16:00	7AC27XX	3.00E+12	1.44E+11	7.40E-03	9.50E-04	3.77E+10
13:16:49	4SX32XX	3.20E+11	1.54E+10	5.00E-03	-5.10E-03	5.91E+10
13:17:03	BT353XX	3.10E+12	1.49E+11	9.80E-03	-5.50E-03	2.55E+11
13:17:29	5SH55XX	4.30E+12	2.06E+11	1.00E-02	6.00E-02	2.97E+08
13:17:42	1AH35XX	2.80E+12	1.34E+11	3.30E-02	9.50E-04	8.78E+07
13:18:02	2S801XX	6.90E+10	3.31E+09	9.30E-03	5.60E-04	5.48E+14
13:18:16	3SD64XX	1.40E+10	6.72E+08	2.10E-03	1.30E-01	3.32E+14
13:18:34	7M281XX	2.80E+11	1.34E+10	1.80E-02	7.00E-04	2.63E+11
13:19:23	4SP44XX	4.90E+10	2.35E+09	2.60E-03	1.20E-05	2.12E+15
13:19:39	7A497XX	2.70E+13	1.30E+12	8.20E-03	1.00E-03	4.62E+09
13:20:02	3SL48XX	2.10E+12	1.01E+11	4.00E-03	-5.50E-03	3.79E+11
13:20:34	7J167XX	2.00E+12	9.60E+10	5.40E-03	1.10E-03	1.05E+11
13:22:13	5SU92XX	1.00E+12	4.80E+10	5.70E-03	2.00E-03	1.59E+07
13:22:46	5SC26XX	2.30E+12	1.10E+11	1.00E-02	6.60E-04	1.22E+09
13:24:04	1SU32XX	1.90E+11	9.12E+09	2.90E-03	1.50E-02	4.12E+10
13:26:30	7P131XX	5.20E+10	2.50E+09	2.70E-03	6.30E-04	1.73E+10
13:28:40	9U691XX	2.30E+12	1.10E+11	3.60E-03	3.70E-03	1.17E+14
13:30:11	7AS03XX	3.40E+10	1.63E+09	1.10E-02	2.60E-04	3.03E+12
13:31:37	3S527XX	6.40E+11	3.07E+10	5.00E-03	-1.00E-05	1.32E+11
13:32:32	AKR65XX	1.60E+13	7.68E+11	8.50E-03	-4.80E-03	1.65E+08
13:33:01	2AY70XX	3.60E+11	1.73E+10	4.20E-03	3.70E-03	9.84E+10
13:35:18	7U577XX	5.70E+12	2.74E+11	6.10E-03	6.50E-04	3.14E+11
13:35:34	8C336XX	2.70E+13	1.30E+12	8.10E-03	8.80E-03	2.64E+09
13:35:46	2SJ69XX	5.00E+10	2.40E+09	8.10E-03	3.80E-03	5.65E+09
13:36:33	8A418XX	4.80E+12	2.30E+11	4.50E-03	-6.10E-03	6.34E+06
13:37:29	2AS48XX	7.40E+11	3.55E+10	-2.10E-02	-6.60E-03	1.66E+12
13:37:43	3SX00XX	6.00E+12	2.88E+11	-1.60E-03	-1.00E-03	7.51E+08
13:38:16	4L967XX	5.00E+11	2.40E+10	3.30E-03	-5.40E-04	1.66E+11
13:40:08	7C600XX	3.10E+12	1.49E+11	8.10E-03	-6.50E-03	7.24E+11
13:40:17	4AS60XX	8.70E+11	4.18E+10	-5.00E-04	-5.30E-04	3.10E+07
13:42:17	4AV20XX	3.10E+11	1.49E+10	6.80E-04	7.70E-03	6.68E+13
13:42:32	7S734XX	3.10E+12	1.49E+11	-8.20E-03	-1.60E-03	1.62E+10
13:42:57	1AX59XX	1.60E+11	7.68E+09	-5.30E-04	1.60E-01	3.59E+11
13:43:19	7A102XX	3.30E+12	1.58E+11	-4.30E-04	1.40E-03	6.29E+14
13:43:32	9S990XX	1.50E+11	7.20E+09	-6.90E-04	-1.20E-03	1.57E+11

13:44:52	8P690XX	2.80E+12	1.34E+11	5.20E-03	-6.70E-03	1.48E+13
13:45:07	7AD88XX	3.00E+12	1.44E+11	6.40E-03	-6.60E-03	6.55E+08
13:46:38	3AH78XX	9.90E+11	4.75E+10	4.40E-03	-5.30E-04	1.21E+11
13:47:14	2SI66XX	1.80E+12	8.64E+10	-3.00E-04	-1.00E-03	2.10E+12
13:47:24	8T891XX	9.80E+11	4.70E+10	9.50E-03	-4.90E-04	2.49E+14
13:47:33	3SY58XX	3.30E+10	1.58E+09	7.50E-03	6.90E-05	2.29E+12
13:47:44	3SH64XX	3.30E+12	1.58E+11	6.50E-03	-4.40E-04	6.83E+10
13:48:09	4SM28XX	7.20E+11	3.46E+10	-3.90E-04	-6.50E-03	9.78E+14
13:48:34	6AN15XX	2.70E+12	1.30E+11	1.10E-02	-5.60E-04	2.14E+14
13:49:16	8AM64XX	1.10E+13	5.28E+11	1.60E-03	4.90E-03	1.16E+10
13:50:56	5P79XX	1.00E+12	4.80E+10	6.00E-03	-6.50E-03	7.28E+11
13:51:31	1BT15XX	2.80E+12	1.34E+11	1.30E-02	-1.10E-03	1.46E+09
13:54:38	4K423XX	7.10E+10	3.41E+09	2.10E-03	3.00E-02	4.90E+10
13:54:50	5SE31XX	1.30E+12	6.24E+10	1.80E-03	-5.40E-04	7.68E+10
13:55:13	8P237XX	3.20E+11	1.54E+10	-1.40E-04	3.60E-02	3.31E+11
13:56:21	1A004XX	3.10E+12	1.49E+11	9.30E-03	-6.50E-03	3.87E+08
13:58:53	2SH44XX	1.80E+12	8.64E+10	1.50E-01	-5.70E-03	1.14E+08
13:59:22	1UD95XX	7.90E+11	3.79E+10	1.50E-01	-5.30E-04	7.12E+14
14:01:58	7AZ18XX	3.60E+11	1.73E+10	1.60E-03	7.00E-03	4.32E+14
14:02:05	1SJ77XX	1.60E+11	7.68E+09	4.00E-02	1.20E-01	3.42E+11
14:02:12	8AC12XX	1.00E+12	4.80E+10	4.80E-03	-6.60E-03	2.76E+15
14:03:45	3SU14XX	1.20E+13	5.76E+11	8.20E-03	1.40E-02	6.01E+09
14:06:07	8AJ28XX	7.70E+11	3.70E+10	2.40E-03	-6.50E-03	4.93E+11
14:07:04	6AT90XX	7.40E+12	3.55E+11	4.00E-03	-6.10E-03	1.36E+11
14:07:10	3SH89XX	4.20E+11	2.02E+10	8.30E-03	9.80E-03	2.06E+07
14:07:32	3AA36XX	6.50E+11	3.12E+10	8.90E-03	-2.90E-03	1.58E+09
14:08:46	9U615XX	2.10E+12	1.01E+11	-7.20E-04	8.10E-03	5.36E+10
14:09:12	2SB40XX	2.80E+12	1.34E+11	3.90E-03	-9.80E-04	2.25E+10
14:12:54	1BT96XX	5.80E+12	2.78E+11	8.10E-03	1.20E-02	1.52E+14
14:16:50	L666XX	2.10E+12	1.01E+11	2.70E-02	7.10E-03	3.94E+12
14:18:34	5AF03XX	1.20E+13	5.76E+11	8.10E-03	-2.20E-03	1.72E+11
14:19:36	5SM94XX	1.60E+13	7.68E+11	4.80E-03	1.60E-01	2.15E+08
14:20:36	6J714XX	1.70E+12	8.16E+10	2.40E-03	8.30E-04	1.28E+11
14:21:39	2SP21XX	5.80E+12	2.78E+11	7.20E-03	-1.70E-03	4.08E+11
14:22:29	9AC78XX	6.80E+12	3.26E+11	7.50E-03	-7.20E-03	3.44E+09