# The Effect of Diesel Fuel Sulphur and Vanadium on Engine Performance and Emissions

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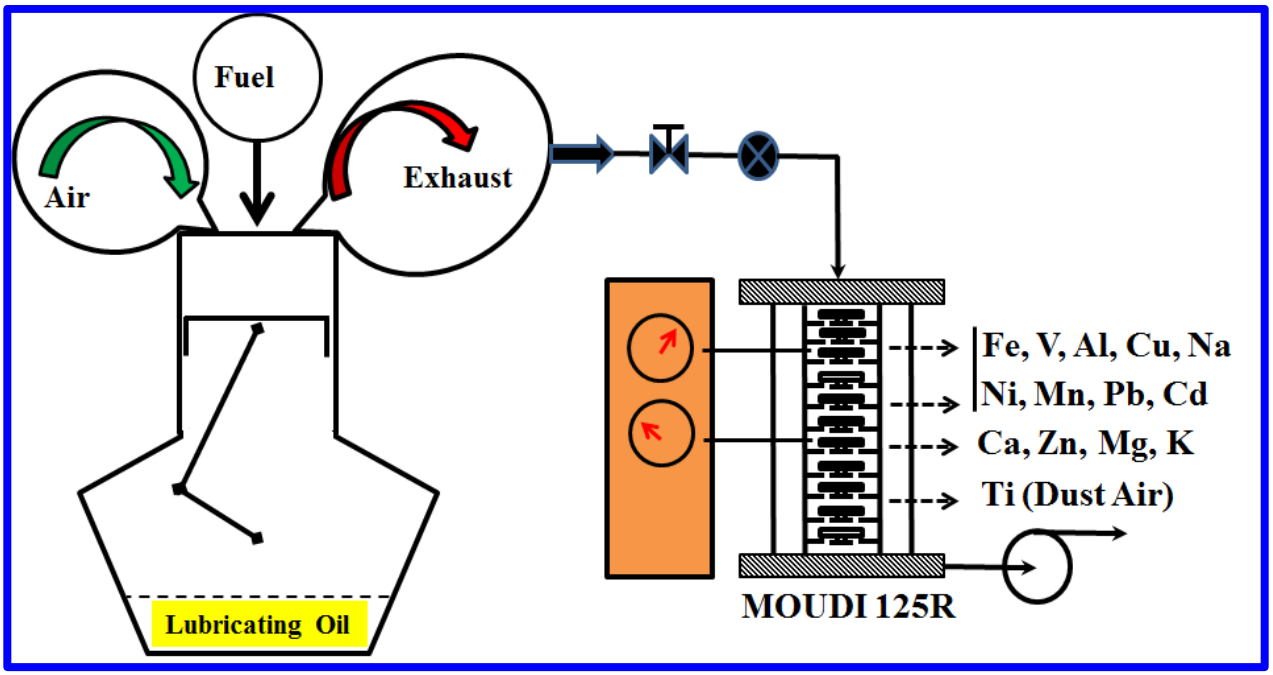
## HIGHLIGHTS

- Source identification of metallic elements in the engine exhaust particles performed;
- Metallic element distributions in exhaust measured at different particle size fractions;
- Lubricant related metals contributed to metallic solid ultrafine particles (Dp < 100 nm);
- Fuel and engine wear related metals dominant in the accumulation particle mode;
- Large impacts of engine load on $NO_x$ and fuel S content on PM were found;

## GRAPHICAL ABSTRACT





## ABSTRACT

Metallic composition of diesel particulate matter, even though a relatively small proportion of total mass, can reveal important information regarding engine conditions, fuel/lubricating oil characteristics and for health impacts. In this study, a detailed investigation into the metallic elemental composition at different particle diameter sizes has been undertaken. A bivariate statistical analysis was performed in order to investigate the correlation between the metallic element, measured engine performance and engine emission variables. Major sources of metallic elements in the emitted particles are considered in this study, including the fuel and lubricating oil compositions, engine wear emissions and metal-containing dust in the ambient air. Metallic solid ultrafine-particles (Dp < 100 nm) are strongly associated with metallic compounds derived from lubricating oil (Ca, Zn, Mg and K), while the fuel related metallic compounds and engine wear emissions are represented in the accumulation mode particle fraction (> 100 nm). Calculated correlation matrices show a clear effect of engine load conditions and fuel S contents on particle number and mass emissions.



**Key words:** Sulphur, Vanadium, Particle Size Distributions, Metallic Element Distributions, Micro-Orifice Uniform Deposition Impactors (MOUDI).

## 1. Introduction

Marine fuels such as marine diesel oil (MDO) and heavy fuel oil (HFO) are the main fuels used in the shipping industry. This industry accounts for over 80% of global trade by some 90,000 marine vessels [1]. Using low quality marine fuels, owing to their economic benefits [2] significantly contributes to worldwide air pollution and air quality degradation in the vicinity of coastal and port areas [1, 3]. Sulphur (S) and many trace metals and other chemical elements such as silicon (Si), nickel (Ni), iron (Fe), lead (Pb), aluminum (Al), calcium (Ca) and vanadium (V) are observed in marine fuels, so marine fuel combustion consequently results in different compounds like sulfates, organic carbon (OC), elemental or black carbon (EC/BC), ash and heavy metals in emitted particles [4-6], most of which pose a high toxicity risk [7]. It is well documented that inhaling diesel particulate matter is a very significant health risk [8]. Based on a detailed review, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), classified diesel engine exhaust as a carcinogenic substance to human health (Group 1, same as asbestos) [9]. In particular, shipping-related fine particle ($PM_{2.5}$) emissions alone can account for nearly 64,000 cardiopulmonary and lung cancer deaths each year [10]. In Europe, 5–10% of total PM emissions derived from ship emissions corresponded to around 40,000 premature deaths per year [11]. Therefore, quantitative and qualitative research on ship emissions is needed for a deeper understanding for law-makers and regulators [12] and is a matter of critical concern [13].

In the literature, there are three major methods to investigate emissions from ships, namely test-bed, ship plume-based and on-board measurements, in which on-board measurements are essential to fully investigate realistic emission factors [14, 15]. However, a very limited number of on-board measurement studies have been undertaken [13, 16], especially regarding ultrafine particle number, particle chemical composition and the concentration of trace metallic elements in ship exhaust [4, 17]. More fuel parameter-related studies are needed in order to understand emission composition more deeply and to effectively reduce negative health impacts in coastal areas [4]. On-board ship emission measurements are an extremely complex task that needs the participation and availability of a wide range of institutions, as well as modern instruments. Therefore, spiking diesel fuel with S and V is used as an approach to better understand the effect of S and V on engine performance and emissions of auxiliary engines when using fuels containing these components such as diesel or HFO under controlled laboratory conditions [18].

Emissions from ships are regulated by the International Maritime Organization (IMO) through Annex VI of the International Convention for the Prevention of Pollution from Ships – the Marine Pollution Convention (MARPOL). Regulations came into effect on May 19$^{th}$ 2005 introducing limits on the oxides of nitrogen ($NO_x$) and the oxides of sulphur ($SO_x$) emissions in order to reduce harmful pollutants from ships globally. Responding to the desire of some coastal nations for further reduction of $SO_x$ emissions from ships in their regions, Sulphur Emission Control Areas (SECAs) have been instituted by applying provisions contained in the Regulation 14 of MARPOL Annex VI. These regulations limit the marine fuel sulphur content to 0.1% by mass in SECAs by 2015, and to 0.5% globally by 2020. As an alternative to using low- sulphur fuel oil, approved systems for the

abatement of emissions, such as $SO_x$ (wet and dry) scrubbers are likely to be dominantly used [15]. Scrubber systems play a role as filters of the engine exhaust gasses to remove $SO_x$ by using washing-water that will be discharged directly into ocean (open loop), treated with chemicals and reused for a time before discharging (closed loop), or treated through a hybrid mode of the above [19]. Regulation 13 of MARPOL Annex VI controls $NO_x$ emissions from both used and new marine diesel engines that are over 130 kW output power. Different levers or tiers depend upon the ship construction date and engine speed. It should be noted that Tier III requirements apply only to new vessels operating in Nitrogen Oxide Emission Control Areas (NECAs) established to limit $NO_x$ emissions. Exhaust gas recirculation (EGR) arrangements and selective catalytic reduction (SCR) systems seem to be a feasible abatement technology to achieve $NO_x$ reduction. However, a recent study reported that there were around 500-1000 vessels equipped with SCR [20]. This indicates that the large numbers of existing vessels without exhaust cleaning systems are in operation. Therefore, a diesel engine without after treatment system was used in the present study.

The chemical composition and physical characteristics of PM depend on fuel types used, the engine type and engine operating conditions [21]. The most abundant components of PM from marine fuel combustion are hydrated sulfates, OC, EC/BC and trace metals with over 80–97% of total $PM_{2.5}$ mass, in which total trace metals accounted for only 1.25–3.87% [17]. Using the V/Ni ratio as a tracer for a ship's emitted particles (those associated with fuel metal content) is an effective way to detect and assess the contribution of ship emissions to ambient air [7, 22]. While primary PM emission elements of Ca, Zn, P and Mg are largely determined by the composition of lubricating oils [23], OC and EC/BC are affected by engine load conditions [21, 24]. In the literature, the presence of trace metals deposited in emitted PM is poorly investigated [16, 17] and there are few studies concerning metallic elements on particles of different sizes.

In this research, test-bed measurements were performed on a heavy duty, six-cylinder, turbocharged and after-cooled diesel engine with a common rail injection system and without after treatment system in order to provide a detailed insight into the elemental composition at different particle diameter sizes. The engine was tested with spiked diesel fuels with different S and V contents over several engine modes, representing the typical range of in-use operating load conditions. A statistical analysis tool (R studio) was used to calculate correlation matrices investigating relationships between the measured engine performance and emissions variables.

## 2. Methodology

### 2.1. Spiked fuel preparation

Fuel S contents selected were 0.1% and 0.5% (by weight) that relate to S regulations issued by IMO applying in both SECAs and NECAs by 2015, and globally by 2020 respectively. Diesel and HFO contain different S-species associated with the differences in the volatility of the two fuels. Some studies stated that S-containing compounds such as dibenzothiophenes are dominant in HFO [25, 26], and in diesel fuel [27]. In contrast, dibenzothiophenes in alkylated structure were found to be dominant in diesel fuel compared to their parent structure [28]. Therefore, dibenzothiophenes have been selected in this study to spike the fuels with S. Typical trace metals which are commonly found in HFO are V and Fe. V is contained in diesel fuels in a soluble form, which is present as vanadium-porphyrin complexes [29]. The typical concentrations of V in HFO strongly depend upon the source of crude oil. Fe-based fuel-borne catalysts have been widely used in Europe as fuel additives to reduce engine emissions [30]. Chemicals containing these metallic elements (V and Fe) were used to spike the fuels as follows: bis(cyclopentadienyl)vanadium (II) and ferrocene. Further details of fuel preparation can be seen in a previous study [18]. The quantity of these chemicals along with diesel fuel used for spiking fuels can be seen in Table S1 (Supporting Information). Details of these chemicals can be seen in Table S2. The properties of spiked fuels can be seen in Table 1.

**Table 1** Properties of spiked fuels.

| Parameters | Units | Methods | Diesel | S0.1V5 | S0.1V15 | S0.5V5 | S0.5V15 |
|---|---|---|---|---|---|---|---|
| Density | g/L | ASTM D4052 | 837.6[a]<br>844.4[b] | 846[b] | 847[b] | 849[b] | 850[b] |
| Viscosity | $mm^2/s$ | ASTM D445 | 2.66[a]<br>2.66[b] | 3.12[c] | 3.13[c] | 3.32[c] | 3.35[c] |
| Lubricity | mm | IP 350 | 0.41[a] | - | - | - | - |
| Carbon (C) | % mass | - | 87.10[b] | 88.78[b] | 88.72[b] | 88.65[b] | 86.25[b] |
| Nitrogen (N) | % mass | - | 0.054[b] | 0.043[b] | 0.0462[b] | 0.0456[b] | 0.039[b] |
| Sulphur (S) | % mass | - | $6.1 \times 10^{-4}$[a]<br>$7.8 \times 10^{-4}$[b] | 0.097[b]<br>0.095[c] | 0.095[b]<br>0.093[c] | 0.475[b]<br>0.497[c] | 0.513[b]<br>0.512[c] |
| Vanadium (V) | mg/kg | - | <1[c] | 4[c] | 13[c] | 5[c] | 14[c] |
| Iron (Fe) | mg/kg | - | <1[c] | 8[c] | 8[c] | 8[c] | 8[c] |
| HHV* | MJ/kg | ASTM D240 | 45.64[b] | 44.16[b] | 44.31[b] | 43.34[b] | 43.68[b] |

([a] from CALTEX, [b] tested at QUT; [c] from Hasting Deering; * Higher heating value)

### 2.2. Engine specifications and experiment set-up

This experimental investigation used a heavy duty, six-cylinder, turbocharged, after-cooled diesel engine with a common rail injection system located in the Biofuel Engine Research Facility (BERF) at the Queensland University of Technology. The exact specifications of this engine are presented in Table 2. Further details of the engine specifications can be seen in previous studies [18, 31]. The research engine was tested at a constant speed (1500 rpm) and two engine load conditions (25% and 50% load) which are typical operating conditions of an auxiliary marine engine. Higher engine loads up to 80-90% were not carried out due to the limitations of time and costs of chemicals for spiking fuels. Paper filter was used at the intake air of the engine. Fig. 1 shows a schematic diagram of the experimental setup. The first sampling point was used for raw exhaust measurements

by a Testo 350 XL for gaseous concentration including sulphur dioxide ($SO_2$), nitrogen oxides ($NO_x$), carbon monoxide (CO), carbon dioxide ($CO_2$), oxygen ($O_2$), and unburned hydrocarbons (HCs). The raw hot-exhaust was also directed to the DMS500 MKII Fast Particulate Spectrometer (CAMBUSTION, Cambridge, UK) after a two-stage dilution system (in-built into the instrument) and the CAI $NO_x$ and $CO_2$ analysers measured from the second sampling point. Particle number size distributions in the size range of 5 nm–1.0 μm were analysed with a sampling frequency of 1 Hz using a DMS500 MKII through a heated sample line, and two dilution stages. The third sampling point was firstly diluted through the dilution tunnel and then used for measurements with a Micro-Orifice Uniform Deposit Impactor (MOUDI 125R Impactor, MSP Corporation, USA), a DustTrak™ and a Sable CA-10 carbon dioxide analyser. The MOUDI 125R is a 13-stage cascade impactor that works on the principle of inertial impaction combined with PTFE Teflon filters for off-line metal concentration measurements for the emitted particles. A DustTrak™ II Aerosol Monitor 8530 (TSI), which is a light-scattering laser photometer giving real-time aerosol mass readings, was used to measure mass concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$. Raw and dilute $CO_2$ measurements were used to determine the sample dilution ratios (DR) for the DustTrak™ measurments. Further details on the dilution condition are provided in Table S3. A flow rate of 10 L $min^{-1}$ was fixed for MOUDI 125R sampling, created by a vacuum pump. Details of the sampling line length and flow rate for other instruments can be seen in Table S4.

**Table 2** Test engine specifications

| **Item** | **Specification** |
|---|---|
| Model | Cummins ISBe220 31 |
| Cylinders | 6 in-line |
| Capacity (Litres) | 5.9 |
| Bore x Stroke (mm) | 102 x 120 |
| Maximum Torque | 820 Nm @ 1500 rpm |
| Maximum Power | 162 kW @ 2500 rpm |
| Compression Ratio | 17.3:1 |
| Aspiration | Turbocharged (waste gated) & after cooled |
| Injection Type | High pressure common rail |
| Dynamometer Type | Electronically controlled water brake dynamometer |
| Emission Standard | Euro IIIA |

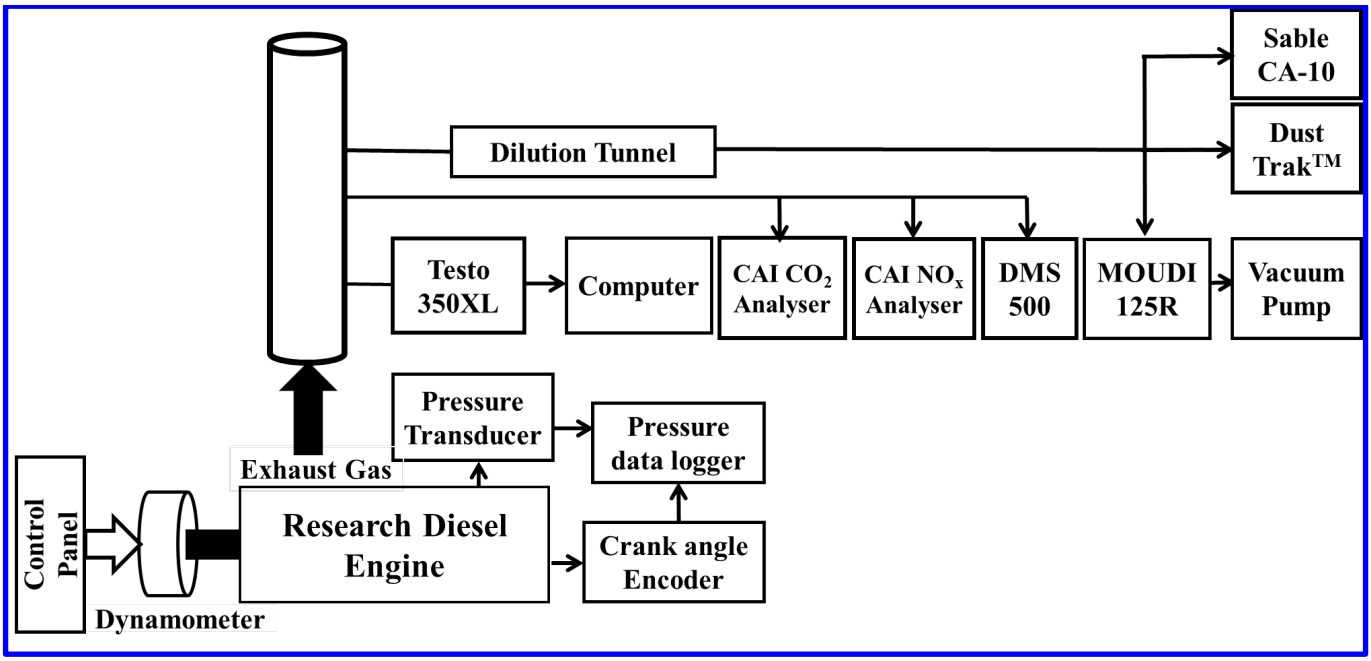



**Fig. 1.** Schematic diagram of experiment setup

### 2.3. MOUDI sampling setup and chemical analytical methods

Measurements of the particle mass distribution were done through a 13-stage cascade impactor that works on the principle of inertial impaction [32]. The schematic for particle collection with the MOUDI can be seen in the Supporting Information (Fig. S1). MOUDI impactor classifies particles based on their aerodynamic diameter that is affected by the effective density of particles. The MOUDI was configurational for particulate matter collection in four size fractions (< 10 nm, 10–100 nm, 100–1000 nm, and > 1000 nm). The last stage < 10nm was collected on the backup filter. Due to the characteristics of this instrument the smallest (10 nm) cut-off cannot be known with great precision. The modification of MOUDI can be found in previous studies [33, 34]. The sample was collected for 25 min and deposited on 47 mm diameter 0.45 µm pore Teflon (PTFE) filters (Pall Life Sciences, Ann Arbor, MI). One-eighth of the Teflon filter was initially digested by microwave digestion in a 30 mL mixed acid solution ($HNO_3$: $HClO_3$ = 3:7) by heating it up to 150–200 $^0$C for 2 hours to extract metals from the collected particles. After the digestion, 50 mL de-ionized (D.I) water was added to the residual solution for metallic content analysis. Seventeen metallic elements consisting of As, Ca, Cd, Cr, Cu, Fe, Mg, Na, Mn, Sb, Ni, Pb, Ti, V, Al, K, and Zn were analysed with an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES; Perkin Elmer, Model Optima, 2000DV). In order to prevent background contamination in the engine lab, the operational blanks (unexposed filters) were used simultaneously with the exhaust samples. The blank interference was ignored in the present study because of its insignificance found. This chemical analysis was carried out in the Air Pollution Laboratory at National Sun Yat-sen University. The quality assurance and quality control of chemical analysis that were conducted in this study are described in more details in the Supporting Information (Table S5). Further details of this method can also be seen in a previous study [35].

177

178 **2.4. Datasets and their analysis**

179 **2.4.1. Correlation matrices**

180 Correlation matrices were calculated in R [36] to explore the relationship between variables in this study.
181 Correlation co-efficients (*r*) lie on the interval [-1 1] and are calculated in a pairwise manner for every
182 combination of variables. An r value of 1 indicates perfect correlation, r=-1 indicates perfect anti-correlation for
183 a variable pair, whereas an r value of 0 indicates no relationship. Calculations were performed using the corrplot
184 package [37].

185

186 **2.4.2. Datasets analysed**

187 Correlation matrices were calculated in R for two datasets. The first dataset involved the particle-phase metallic
188 concentrations resulting from ICP-AES, while the second dataset analysed the complete dataset consisting of
189 gas and particle phase pollutants as well as engine performance variables. Information regarding replication was
190 retained in analyses of both datasets.

191

192 **3. Results and discussion**

193 **3.1. Identifying sources of metallic elements in the engine exhaust particles**

194 Fig. S2 shows obvious potential sources of metals in the particles emitted from the diesel engine exhaust. They
195 come mostly from the composition of fuel burned, lubricating oil used, ambient air and engine wear. Source-
196 specific information should be obtained to determine and confirm directly the major sources of metallic elements
197 in the emitted diesel engine exhaust particles. In particular, seventeen metallic elements consisting of As, Ca,
198 Cd, Cr, Cu, Fe, Mg, Na, Mn, Sb, Ni, Pb, Ti, V, Al, K and Zn from diesel engine exhaust emissions were collected
199 on Teflon filters and were analysed by using ICP-AES. The results of this analysis consisting of different spiked
200 fuels and engine load conditions are presented in Fig. S3. Concentrations of metallic elements from the engine
201 when running reference diesel can be seen in Fig. S4. Elemental analysis for tested fuels, new and used
202 lubricating oil were carried out and the results are presented at Tables S6, S7 and S8 in the Supporting
203 Information. Elemental composition of particles in the ambient air was derived from previous studies [38, 39]
204 and used as a reference in the present study because their work used samples taken in the same city (Brisbane)
205 as this study. The typical metal concentrations in Brisbane ambient air can be seen in Table S9, in which the
206 dominant metallic elements in the ambient air (presented in the red text) are Na, Fe, Ca, K, Zn, Ti and Al. It
207 should be noted that PM concentration and composition in the engine laboratory (in the present study) may
208 differ from that of these studies, which sampled PM at inside schools, outside at suburban areas and roadsides.
209 Therefore, the reference may partly reflect the real world situation.

210

211 **3.2. Correlation of metallic variables in the engine exhaust emissions**

212 Fig. 2 shows the correlation of metallic elements in the engine exhaust emission. In particular, the scale bar is
213 the correlation coefficient (from -1 to 1), the blue symbol indicates that these variables are correlated while the

red one represents the anti-correlated variables. In addition, size of symbol illustrates the strength level of correlation/anti-correlation, for instance, larger circle means stronger their relation is. There are ninety-two samples in total including all of the engine load conditions (25 and 50%) and tested fuels, which were used to plot Fig. 2. Based on the interpretation of Fig. 2, it can be seen clearly that there are three separate groups of variables. Correlated variables included Ca, Zn, Mg and K are strongly associated with lubricating oil, while elements related to the fuel composition (V, Fe) and engine wear (Fe, Al, Cu, Cr, Pb and Cd) are found in the same group. Pb and Cd have been reported from engine wear, most likely from piston rod bearings [40, 41]. The last group with elements such as As and Ti that is most likely to be from air dust source or/and engine cylinder walls. The reason for the present of As in the air is not clear but it is consistent with a previous study [42] who found As in combustion particles near airport in both large and small sizes. In addition, as be seen in Fig. 2 that a correlation between As and Ti which is most likely to prove the evidence of As in the air. However, further work is needed to confirm scientifically this statement because this correlation observed in the present study is weak (the correlation coefficient of around 0.2-0.25).

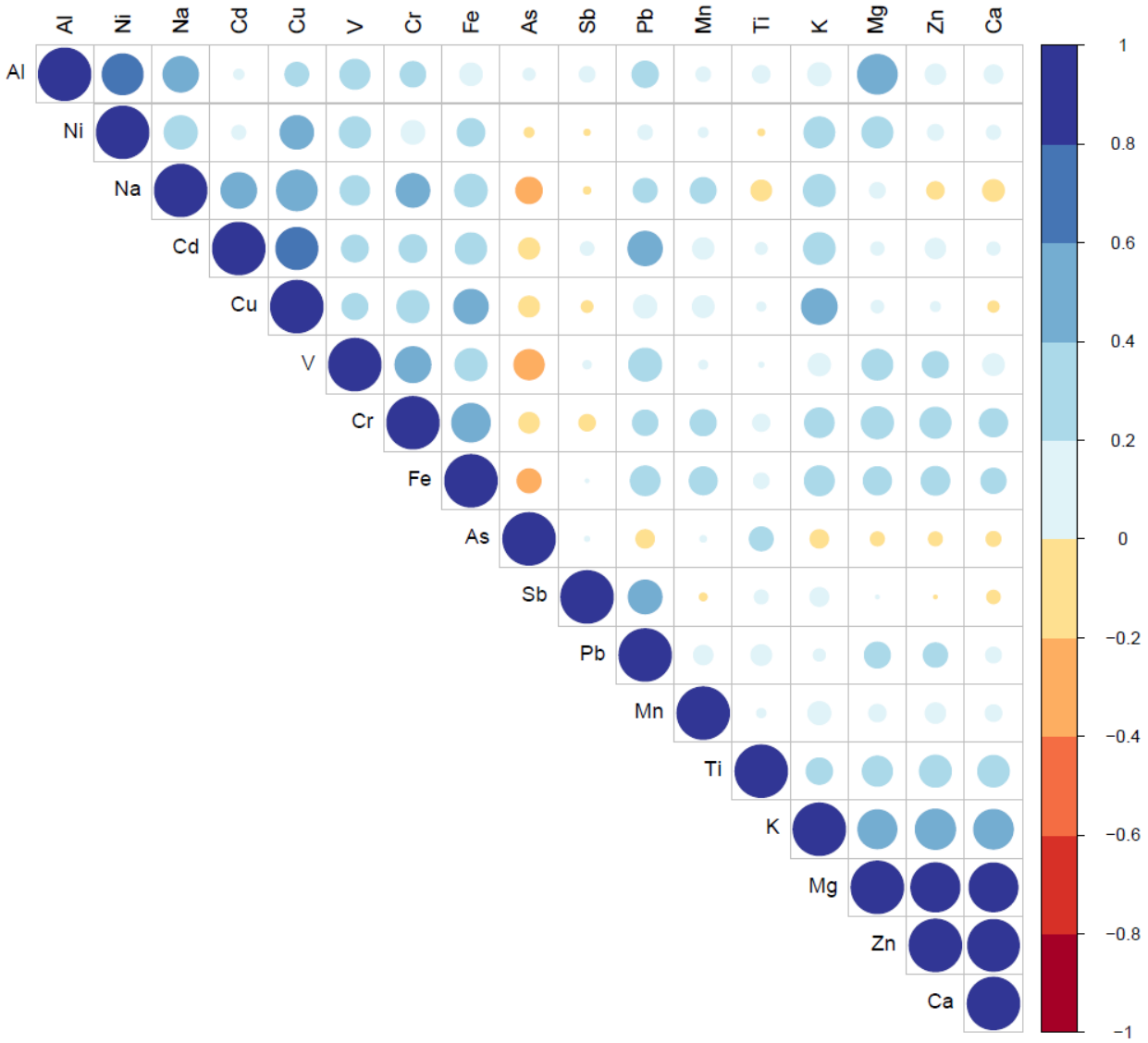



**Fig. 2.** Correlation matrix of particle phase metallic concentration variables in the engine exhaust emission

Fig. 3 shows the metallic element concentrations distributed at four different MOUDI stages including different particle aerodynamic diameters (Dp < 10 nm – stage 1; 10 nm < Dp < 100 nm – stage 2; 100 nm < Dp < 1000 nm – stage 3; Dp > 1000 nm – stage 4). The results at each MOUDI stage were averaged for the all of engine load conditions and tested fuels in the total of ninety-two samples. MOUDI stages 1, 2, 3 and 4 presented in green, blue, red and black columns, respectively. Based on Fig. 3, the concentration of particular metallic element varies greatly with different MOUDI stages. In particular, it is clearly evident that metallic elements derived from lubricating oil in the emitted particles are strongly associated with the MOUDI stages 1 and 2. They are of Ca, Mg, Zn and K which can normally be found as components in engine lubricating oil (Table S7). It can be concluded that metallic solid ultrafine-particles (Dp < 100 nm) of diesel exhaust mainly originate from metallic contents in the lubricating oil. The results in the present study are also in agreement with previous studies for both gasoline engines [43, 44] and diesel engines [45, 46]. A recent study [47] also found that lubricating oil was a major component of ship exhaust particle emissions.

Fuel-related metallic contents and engine wear emissions such as Fe, Na, Al and Pb are mainly dominant at MOUDI stages 3 and 4. It is most likely to be that particles larger in diameter (> 100 nm) are strongly associated with fuel-related metallic contents and engine wear emissions. Other metallic elements such as As and Ti show a significant distribution to the MOUDI stage 1 which represents the smallest particles (Dp < 10 nm). Therefore, it can be concluded that the smallest particles (Dp < 10 nm) are most likely to be linked with elements from the combustion of dust in the air such as Ti and As. However further work is required to confirm this hypothesis because any particles < 10 nm would have a different origin to the larger ones as their composition and formation mechanisms are significantly different.

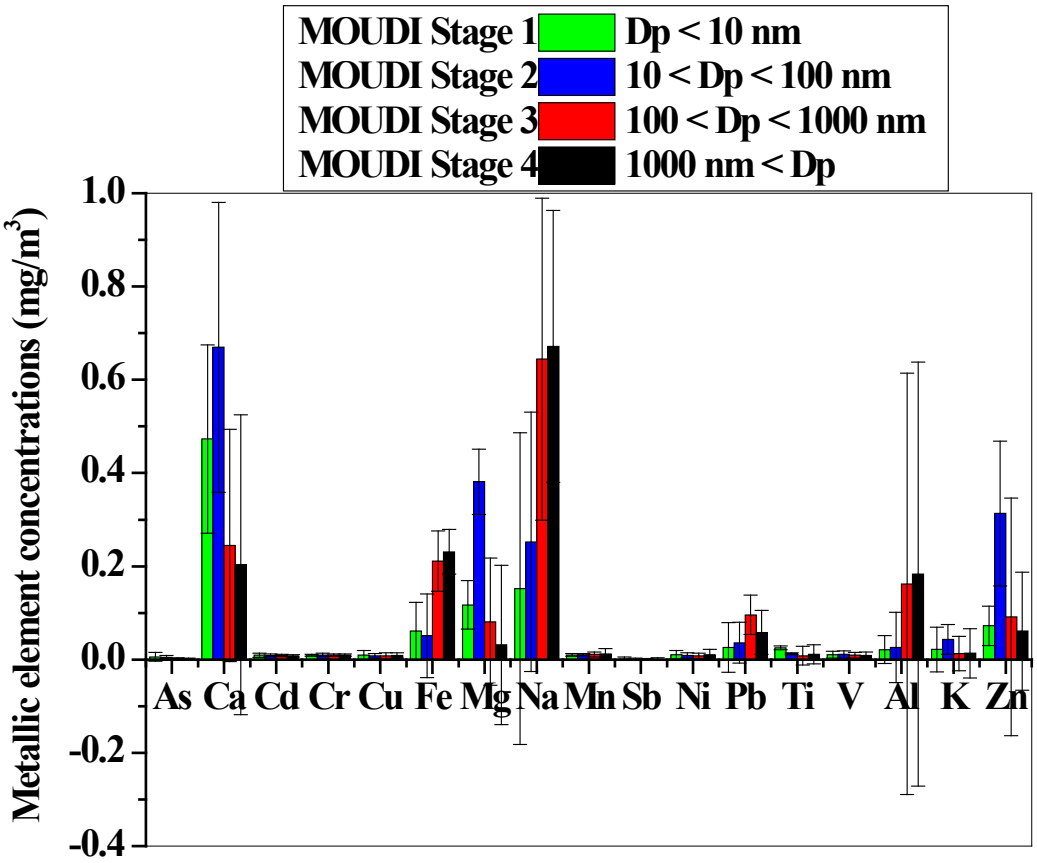



**Fig. 3.** Metallic element concentration distributions at different MOUDI stages. The results at each MOUDI stage were averaged for the all of engine load conditions and tested fuels in the total of ninety-two samples.

### 3.3. The correlation between the measured engine performance and emission variables

Fig. 4 shows the correlation between the measured engine performance and emission variables where Table S10 provides a full listing of the abbreviations used for variables, along with their units. However, it should be noted that metallic element concentrations are in $mg/m^3$. All of engine load conditions (25 and 50%) and tested fuels in the total of twenty-three samples were used to plot this figure. Fig. 4 shows that the group of variables including indicated power (IP), indicated mean effective pressure (IMEP), maximum in-cylinder pressure (P_PRESS), $NO_x$ and engine blow-by (BBY) are strongly correlated. It is clear that higher engine loads resulted in an increase in engine combustion chamber temperature and pressure, consequently leading to higher $NO_x$ emissions and a larger flow of exhaust gas leaking (blow by) through the engine piston rings into the engine crankcase. Anti-correlated variables with these in the above-mentioned group consist of $O_2$, $CO_2$, particle number concentration in the accumulation mode (PNC_ACC), total particle number concentration (PNC), $SO_2$, CO, $PM_{2.5}$ and particle mass measured by the DMS500 (PM_DMS). These variables are believed that having a strong association with low engine load condition which typically represents sub-optimum working conditions. These conditions can lead to incomplete combustion, consisting of both partially burnt fuel and lubricating oil, leading to increased concentrations of CO and particle mass and number concentration. This result is in agreement with previous on-board ship emission measurements [14]. Interestingly, $O_2$ shows an inverse correlation $NO_x$ and a correlation with $CO_2$ as can be seen in Fig. 4. It is expected that a direct correlation between $O_2$ and

$NO_x$ as invested in a previous study [2] and an inverse correlation between $O_2$ and $CO_2$ as found in our previous work [14]. However, the presence of high levels of S in the fuel is well known to significantly alter all emissions because of the presence of $SO_x$, which acts as a sink for $O_2$ and supports increased particle formation.

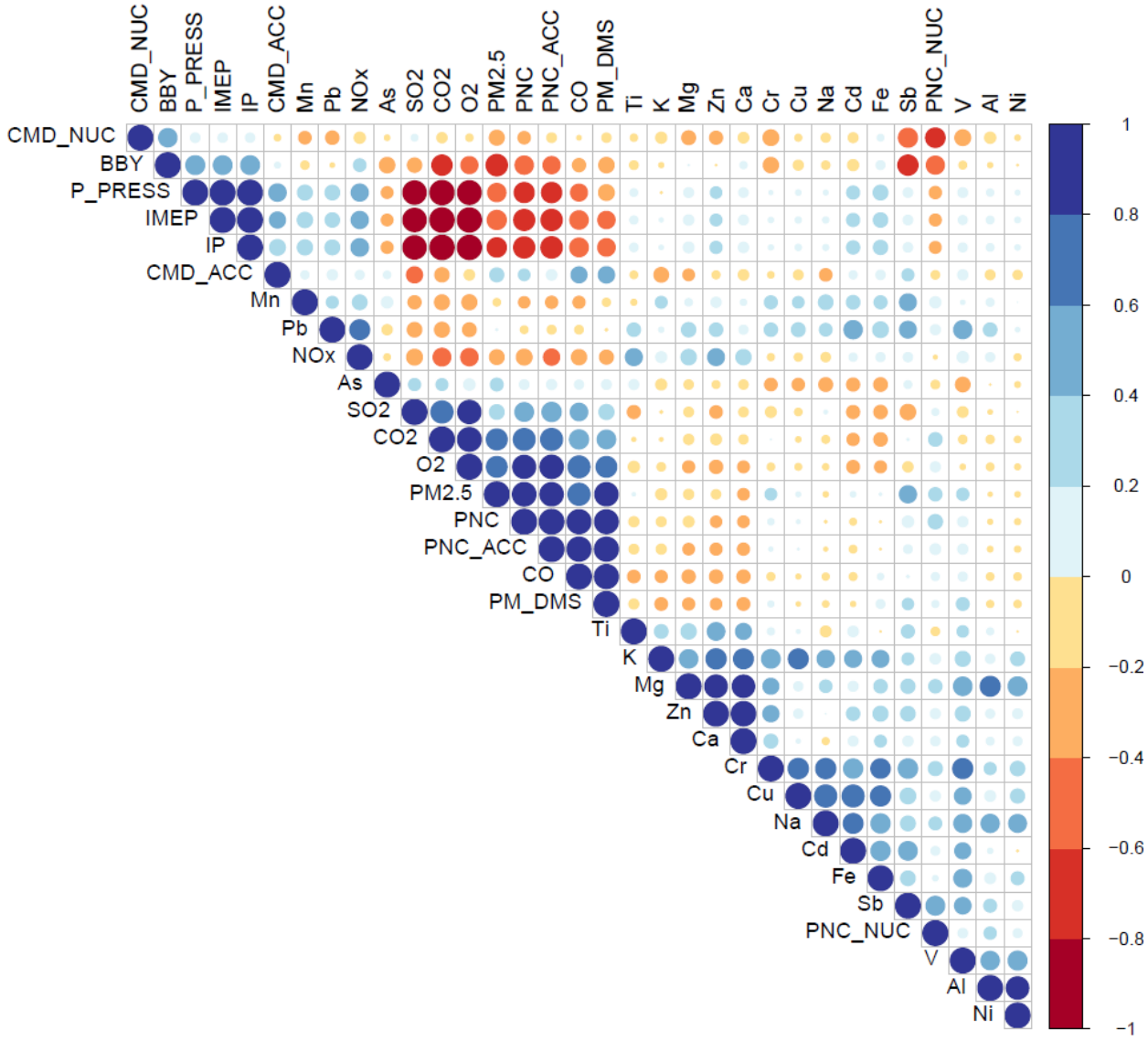



**Fig. 4.** Correlation matrix of measured engine performance and emission variables. All of engine load conditions (25 and 50%) and tested fuels in the total of twenty-three samples were used to plot this figure.

Fig. 4 also indicates a strong link between high fuel S content and particulate matter. Higher fuel S content generally resulted in higher $SO_2$ emissions which show a correlation with particle mass and number emissions. In addition, fuel S content S and BBY are anti-correlated on Fig. 4. High S content in the fuel is associated with higher viscosity and lubricity, as shown in Table 1. Such higher viscosity is linked to lower engine blow-by because a better seal against combustion gas leakage will be achieved on the piston rings and the piston-cylinder interaction generally [48]. A positive correlation of engine blow-by and IP, IMEP and P-PRESS is clearly observed in Fig. 3, which is completely consistent with normal engine operation.

### 3.4. Particle sized distributions

Fig. 5 shows the particle number and mass size distributions for tested fuels at two different engine load conditions (25 and 50%). Relative concentration results for both PN and PM to the reference diesel at 25% load were used in the present study in order to investigate the effects of fuel compositions (S and V contents) and engine load conditions. It can be seen in Fig. 5 that bimodal for particle number size distributions were observed for the tested fuels containing S content. No particles in nucleation mode were found in the reference diesel. Higher PN and PM concentrations observed for the spiked fuels than diesel, are most likely due to the fuel S and V content. These fuel components will be burned to form sulphur and vanadium oxides which are attributed to an increase both PN and PM. This is in agreement with correlation results presented in Fig. 4, which show a correlation between fuel (S and V) content and particulate matter emissions (PN and PM). Fig. 4 also shows a strong effect of engine load conditions on particle emissions. Higher engine load condition results in lower particle number and mass emissions. Effects of engine load conditions on exhaust particle emissions also discussed thoroughly in the present study (Section 3.3). The PN concentration in #/cm$^3$ and PM in mg/m$^3$ at two different engine load conditions (25 and 50%) can be seen in a previous study [18].

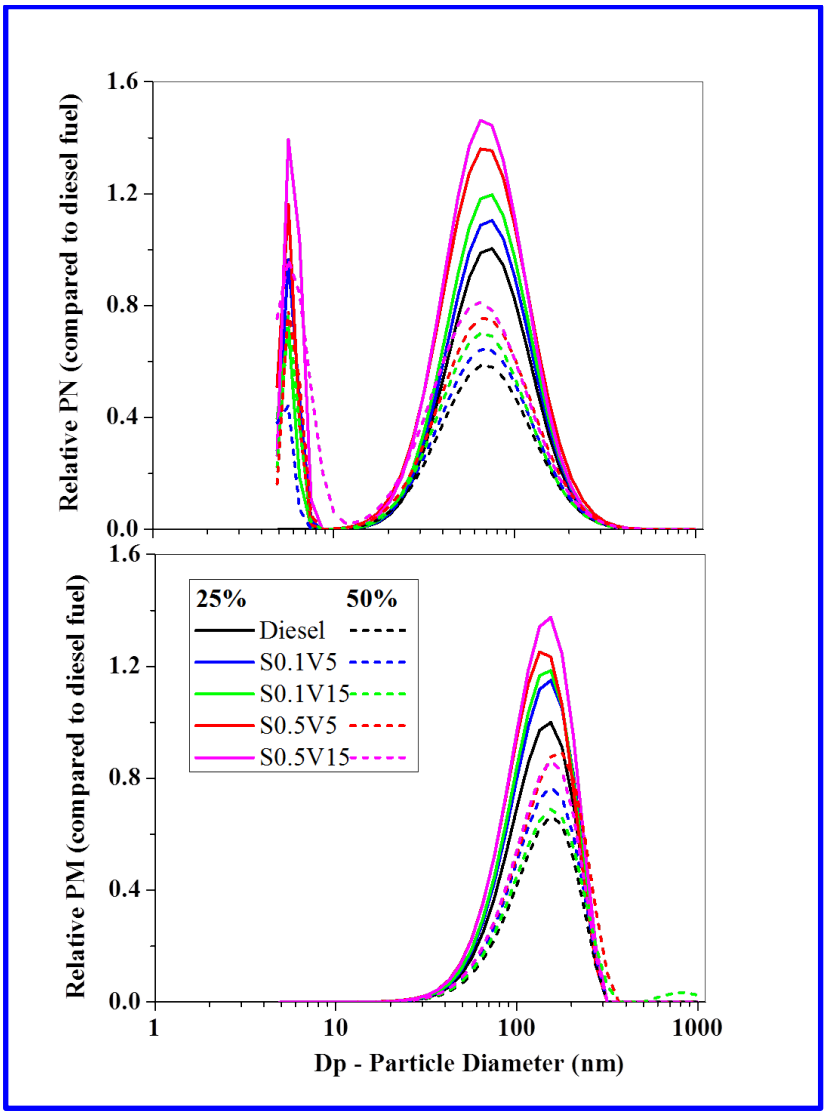



**Fig. 5.** Relative particle number and mass size distributions for reference diesel and spiked fuels at different engine load conditions (25 and 50%).

## 4. Conclusions

This study clearly showed that the most sources of metallic elements in diesel particulate matter emissions originate from fuel, lubricating oil, engine wear and ambient dust in the air. Metallic solid ultrafine-particles (Dp < 100 nm) are strongly associated with metallic compounds derived from lubricating oil (Ca, Zn, Mg and K), while the fuel related metallic compounds and engine wear emissions are represented in the accumulation mode particle fraction (> 100 nm). Air Dust related metallic element concentrations (As, Ti) are low but they are linked to the significant contribution to the smallest particles (Dp < 10 nm). Correlation matrices were calculated in order to investigate the correlation between variables such as metallic elements, the measured engine performance and engine emission parameters. It was found that there was a strong effect of engine load conditions on particle number and mass emissions. Moreover, results from the present study also indicate a strong link between high fuel S content and particulate matter.

**Acknowledgements**

The first author gratefully acknowledges the financial support from the Government of Vietnam for a PhD scholarship. The authors would also like to acknowledge: the software developer, Mr. Andrew Elder from DynoLog Dynamometer Pty Ltd; laboratory assistance from Mr. Noel Hartnett; QUT staff and colleagues for their support and guidance. In addition, we gratefully acknowledge the anonymous reviewer who suggested the use of the correlation matrix for this analysis.

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at https://www.journals.elsevier.com/fuel

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