



Diesel/biofuel exhaust particles from modern internal combustion engines: Microstructure, composition, and hygroscopicity



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HIGHLIGHTS

- Diesel/biofuel combustion emissions from modern internal combustion engines are analyzed.
- Particulate microstructure is revealed in soot and fly ash groups as well as their hygroscopicity.
- Most polluting conditions with respect to fouling of the exhaust system are indicated.
- Multicomponent composition is impacted by both fuel and operation conditions.

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ABSTRACT

Changes in fuel characteristics and design of diesel engines have been applied in the last decades to reduce pollutant emissions in the transportation sector. Characteristics of exhaust particles and their environmental impacts need to be brought up to date. In this study, diesel and rapeseed oil were used in modern internal combustion engines (BMW and John Deere) in order to simulate stationary and transient non-road driving conditions, with attention on fouling processes in the exhaust system and contributions to atmospheric pollution. Engine particulate exhaust samples were subjected to individual particle analysis and bulk physico-chemical characterization with respect to polycyclic aromatics, water-soluble organic carbon and inorganic ions. Functionalities of alkanes and oxygen-containing compounds were determined in the exhaust particles. The emitted particles with similar morphology and composition were separated in specific groups, revealing the exhaust microstructure. In-depth characterization of individual particle composition provided insights into the relationship of chemical composition and hygroscopicity, based on fractionation analysis. With improved characterization of diesel/biofuel combustion emissions we demonstrate that the multicomponent composition of modern internal combustion engine exhaust is impacted by both fuel properties and operation conditions.

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1. Introduction

Transport activities contribute around 25% of total anthropogenic emissions of carbonaceous aerosols [1]. Particulate exhaust of transport systems is currently acknowledged to be the

largest source of uncertainties in understanding traffic impacts on the regional environment, while combustion emissions are increasingly recognized as a globally important source of aerosols impacting air quality, visibility, and radiative balance of the atmosphere [2]. Soot particles have significant effects especially in humid environments [3], acting as cloud condensation nuclei (CCN) and thus exerting indirect effects on haze formation and wet deposition, by instigating longer cloud lifetimes and higher cloudiness. In urban areas diesel engine-emitted particles are considered as a dangerous pollutant with respect to human health because of their high number density, small respirable size, large

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surface area, and potential toxicity. These particles may cause and enhance respiratory, cardiovascular, and allergic diseases [4]. Based on inflammatory responses, hazardous substances were found in diesel-emitted particles [5], while risks associated with specific chemical particle constituents remain uncertain. Most previous studies have aimed to obtain information on average chemical characteristics of diesel exhaust particles by bulk analytical techniques. It was found that unburned organic components are condensed on soot particles in various chemical forms dominated by alkanes and polycyclic aromatic hydrocarbons (PAHs), representing from 5% to 90% of particulate matter (PM) mass in dependence of operation conditions [6]. PAH emissions presented irregular results, leading to the hypothesis that the influence of biodiesel source material was particularly strong on the formation of these pollutants. Some increase in light PAHs with biodiesel was observed, becoming the dominant compounds in the exhaust, while nitro-PAHs and oxy-PAHs were reduced with biodiesel blends [7]. Fly ash contains mostly transition and alkali earth metals, as well as water-soluble ionic compounds produced by inorganic contaminants in the fuel, lubricating oil, and engine wear [8–10].

Electron microscopy was developed as a powerful tool for analyses of morphology and composition of individual particles in combustion emissions [11]. Characterization of diesel exhaust was previously done in accordance with morphological specification, such as soot, char, and mineral particles [12]. Soot was found to consist of chain agglomerates of primary particles with a microstructure of graphite microcrystallites [13,14]. Advanced cluster analyses, applied in the on-going studies on modern engine emissions, allows for the grouping of particles, revealing soot and fly ash in the microstructure of diesel engine exhaust [15,16].

The general assumption that diesel exhaust soot is insoluble and therefore poor CCN [17] was based on elemental carbon (EC) and hydrophobic alkanes dominating the composition of traffic-emitted particles, while the contribution from hydrophilic oxidized organics and sulfuric acid was found to be small [10]. Analysis of water interaction with soot of various composition, from EC to complex mixtures with water-soluble compounds, significantly improved the association between soot physico-chemistry and CCN formation, indicating that C–H and oxygen-containing functionalities are related to hydrophobic and hydrophilic surfaces, respectively, while the presence of water-soluble compounds leads to soot hygroscopicity [18,19].

A number of approaches were proposed to differentiate combustion particles at the microscopic level with respect to their ability to take up water. Okada and Hitzenberger [20] separated combustion-derived PM into water-insoluble and hygroscopic particles with and without water-soluble inclusions. The fractionation into C–O, C–O–S, and Me–C–O components of chain soot agglomerates, irregular internally mixed soot, and particles of mineral morphology, respectively, has allowed categorizing particles as hydrophobic, hydrophilic, and hygroscopic [21]. On average, for road traffic emissions, 41% of carbonaceous particles were found to be hydrophobic and 54% of them were separated into hydrophilic and hygroscopic particles.

Important changes in the design of diesel engines have been applied in the last few decades in order to reduce transport pollutant emissions. The effects of engine type and model were emphasized, with major concern on environmental protection by using alternative fuels [22,23]. Biodiesel has been recognized as effective in reducing the exhaust particle mass as compared to conventional diesel fuel [24,25], specifically during various transient/driving cycles [22]. However, improved characterization of diesel/biofuel combustion emissions is needed, specifically for newly designed internal combustion engines and biofuel utilization as alternative fuel to conventional diesel.

This study is devoted to comprehensive physico-chemical and hygroscopic characterization of diesel/biofuel particle exhaust from modern internal combustion engines. First, we differentiate the role of diesel engine operation in regards to the effect of pollutant emissions on fouling in the exhaust system and environmental concern. Furthermore, we highlight the impact of diesel vs biofuel on the particle properties at given operating conditions. Chemical characteristics are inferred from analysis of functionalities, ions, and water-soluble organic carbon. The particles with similar composition and morphology are grouped by cluster analysis to reveal the exhaust microstructure, while the group identification is performed with respect to physico-chemical relevance. Cluster analysis is combined with fractionation analysis here for the first time for categorizing the individual particles with respect to their ability to interact with water in the humid atmosphere.

2. Experimental

2.1. Engine operation and sampling

Two different internal combustion engines were utilized at the Verbrennungskraftmaschinen test bench of the Technical University Munich (TUM). First, a 2 Liter BMW M47D20 4-cylinder engine with a displacement of 1950 cm³ and nominal power of 100 kW was used. Conventional diesel fuel DIN EN 590 with 7% biofuel (Version 2010) was used, with sulfur (S) content of 10 ppm and ash content of 0.01 wt%. The exhaust was diluted with air depending on the operation point of the combustion engine. At the nominal power point of the engine the dilution ratio was 5. The exhaust pipe was isolated and its wall temperature was kept above 180 °C by the usage of heating coils, in order to avoid hydrocarbon condensation. The operation conditions of the exhaust gas heat exchanger were changed by variation of exhaust gas and coolant temperature, as well as the exhaust mass flow. Different adjustments of the engine provided a variation of exhaust composition, especially with respect to total hydrocarbons, PM, and soot which had a major influence upon the fouling behavior. An exhaust-throttle in the exhaust-pipe (i.e., long pipe) was used in order to operate the engine with increased exhaust-backpressure. PM measurements were performed at 1.5 m after the turbocharger of the engine by the CVS (constant volume sampling) method. For particle sampling Pallflex membrane filters EMFAB TX40HI20-WW were used.

The BMW engine met the European emission stage III standard and was suitable to conduct the experiments with the goal to analyze the deposition build-up (fouling) in the tube exhaust gas heat exchanger in dependence on operating conditions of both the engine and heat exchanger. We did not use exhaust gas recirculation (EGR), catalyst or diesel particulate filter (DPF) to analyze the soot deposition and fouling of raw emissions without any exhaust gas after-treatment. Soot concentration was derived from an AVL photoacoustic Micro Soot Sensor. It was found that if the soot concentration in the exhaust was high, the fouling of the exhaust cooler surface by a soot layer build up was extremely fast. Therefore, such conditions are regarded as polluting ones from here on throughout the manuscript. Parameters of the BMW engine stationary operation, such as number of revolutions, break mean effective pressure, fuel mass consumption, and combustion air ratio were varied from 830 to 4000 L/min, 0 to 18.68 bar, 0.6 to 26.28 kg/h, and 1.31 to 3.46, respectively. More than fifty samples were analyzed; a list of diesel stationary (DSB) samples with detailed characterization of the operating conditions is presented in Table 1.

In addition, a John Deere CD6068HL4812 6-cylinder engine was operated. Conventional diesel fuel DIN EN 590 and refined

Table 1

Diesel stationary (DSB) samples from BMW engine exhaust. Engine revolution, break mean effective pressure (BMEP), fuel mass consumption, combustion air ratio (lambda), soot concentration, and PM filter loading are given for each sample. Diesel fuel DIN EN 590 was used for all tests with this engine.

	Revolution (L/min)	BMEP (bar)	Fuel mass (kg/h)	Lambda	Soot (mg/m ³)	PM (mg)
DSB1	4000	15.52	26.28	1.35	52.22	3.00
DSB2	2000	18.68	26.27	1.31	47.96	1.74
DSB3	3000	3.22	6.18	3.46	11.28	0.55
DSB4	1250	6.44	3.71	1.37	430	1.27

rapeseed oil DIN 51605 were used. Filtered fuel-grade oil contained 10 mg/kg of S, 32 mg/kg of alkali earth and phosphorous, and 0.01 wt% ash. Exhaust gas after-treatment and standard EGR-cooling was used during experiments, although we performed the sampling from the exhaust gas before it entered the exhaust gas after-treatment, from the extraction point at 1 m after the engine turbocharger. A list of diesel stationary (DS), rapeseed stationary (RS), rapeseed transient (RT) and diesel transient (DT) samples collected from the John Deere engine at stationary conditions (1–6) and transient (=dynamic) operation cycles (7–8) is presented in Table 2. More specifically, we used a non-road transient cycle (NRTC) which is mandatory since the EPA Tier 4 interim exhaust emission limit for PM certification has been available. The difference between stationary and transient conditions was that in the first case the speed and load did not vary. During both engine operation conditions lube oil 0W30 with low ash content (0.5 wt%), ~2000 ppm of Ca, 670 ppm of P, and 750 ppm of Zn, was used.

2.2. Analysis methods

Fourier-transform infrared (FTIR) spectroscopy complements the molecular level measurements by providing information about functional groups and classes of compounds for the entire aerosol chemical composition. A Shimadzu IRPrestige-21 spectrometer in the diffuse reflectance mode was used. Subtraction of the blank from the sample spectrum was performed by normalization with a band at 1175 cm⁻¹. The difficulty in completely subtracting the strong blank filter bands in the region of 1700–800 cm⁻¹ reduced the utility of this spectral region. Therefore, all spectra interpretations were performed in the regions of 1700–3600 and 540–800 cm⁻¹. The functional groups were identified, along with their corresponding absorption frequencies, according to FTIR databases [26] and authentic chemical standards.

Quantification of individual polar compounds (i.e., mainly carbohydrates) and PAHs was carried out by high-performance anion-exchange chromatography (HPAEC) [27] and gas chromatography with mass-spectrometric detection (GC–MS), respectively, using a Dionex ICS-3000 system and an Agilent HP 6890 GC coupled to a mass spectrometer (MSD model 5973), respectively. For GC analysis, Helium was used as carrier gas at a flow rate

of 1.0 mL min⁻¹ in a capillary column (DB-5) and an injection port temperature of 280 °C. The temperature program started at 50 °C and the oven was programmed to heat up to 120 °C at a rate of 30 °C min⁻¹ followed by a temperature increase to 300 °C at a rate of 6 °C min⁻¹. Filters were put into 4 mL bottles, followed by 2 mL dichloro methane, and ultrasonic agitation was performed for 15 min. Only naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene were detected, and no carbohydrates were detected in any of the analyzed samples. The uncertainty of the PAH analyses, conducted by GC–MS, was estimated to be better than 15% for all species based on replicate analyses of PAH standard solutions.

The following anions and cations were measured by ion chromatography (IC) with conductivity detection: sulfate (SO₄²⁻), nitrate (NO₃⁻), chloride (Cl⁻), phosphate (PO₄³⁻), sodium (Na⁺), potassium (K⁺), calcium (Ca⁺), and ammonium (NH₄⁺). Filter samples were extracted in deionized ultra-pure water by one-hour sonication and filtered through syringe filters (0.45 µm pore size). The cation separation was achieved on a Dionex IonPac CS12 column with a 20 mM methanesulfonic acid eluent at a flow rate of 1.0 mL min⁻¹. Anions were separated on an AS14 column with an eluent composed of 1.7 mM NaHCO₃ and 1.8 mM Na₂CO₃ at a flow rate of 1.2 mL min⁻¹ [27]. While replicate IC analyses of individual samples were not conducted, we estimated the analytical uncertainty of the inorganic ions to be 5%.

Water-soluble organic carbon (WSOC) was measured using an Aurora 1030 W OI-Analytical TOC analyzer. Organic compounds in aqueous sample extracts (same as those prepared for IC analysis) were oxidized in the reaction chamber using heated sodium persulfate (Na₂S₂O₈) at temperatures up to 100 °C. Soluble carbon-containing compounds were oxidized to carbon dioxide which was measured by a non-dispersive infrared (NDIR) gas analyzer. Inorganic carbon was measured by acidifying the sample and converting all carbonates, hydrogen carbonates and dissolved carbon dioxide to carbon dioxide, which was volatilized by bubbling air through the sample. The water-soluble organic carbon was determined as the difference between the total and inorganic carbon. The repeatability of water-soluble organic carbon measurements was calculated as 10% based on replicate analyses of selected samples.

Individual exhaust particles were examined using a LEO 1430-vp (Karl Zeiss) field emission scanning electron microscope (SEM) with a spatial resolution of 7 nm, equipped with an Oxford energy dispersive detector INCA. Particles on the sample filters were examined at 20 kV acceleration voltage under operator control. Energy dispersive X-ray (EDX) spectra including low-Z elements (Z ≥ 5) were recorded in SEM image mode with counting times of 50 s. Approximately 500 individual particles with a diameter from 0.1 to 3 µm were chosen from each sample, sufficient to identify the particle types in each sample [15,28]. The result of EDX analysis was obtained as a data matrix for 20 elements at measured weight concentrations above the detection limit of 0.3 wt%.

Table 2

Diesel stationary (DSJ), rapeseed stationary (RSJ), rapeseed transient (RTJ) and diesel transient (DTJ) samples from John Deere engine exhaust. Operation point, engine speed (n), lambda (air to fuel ratio), torque (T), power (P), and PM loading are provided. Diesel fuel DIN EN 590 and rapeseed oil DIN 51605 were utilized.

	Operation point	n (rpm)	Lambda	T (Nm)	P (kW)	PM (mg)
DSJ-1	D_1300_70	1300	5.60	70.0	9.5	0.23
DSJ-2	D_1300_360	1300	2.31	360.0	49.0	0.24
RSJ-3	RKF_1200_70	1200	5.46	72.0	9.0	0.23
RSJ-4	RKF_1200_360	1200	2.26	360.0	45.2	0.14
RSJ-5	RKF_Idle_2	850	7.98	0.0	0.0	0.14
RSJ-6	RKF_1200_705	1200	1.59	705.0	88.6	0.17
RTJ-7	R_NRTC_V	T	T	T	T	0.92
DTJ-8	D_NRTC	T	T	T	T	2.01

Note: RKF is an intern short cut for experiments performed with rapeseed oil. T means transient.

A combination of hierarchical and non-hierarchical cluster analysis was applied for separation of individual particles on definable groups of similar chemical composition with an accuracy of 3% [29,30]. Final number of groups was proposed when the analysis with lower numbers does not give a good separation with respect to different particle types, while a higher number of clusters leads to duplicate groups with similar composition [15]. The group interpretation was performed using the bulk characterization data. An energy dispersive XRF system (ED-XRF) was used to determine the bulk elemental components from sodium to uranium (Na to U) with a concentration range from ppm to % level.

Fractionation analysis with respect to hygroscopicity was applied for separation of three fractions of carbonaceous particles according to their composition, to allow the quantification of water uptake by soot particles [21]. Both fractions of carbonaceous particles were categorized as hydrophobic, hydrophilic, and hygroscopic. More details of this method are presented elsewhere [21].

3. Results and discussion

3.1. Soot organic composition and microstructure

Functionalities of exhaust particles from the most and least polluting conditions of the BMW engine in stationary operation are shown in the respective IR spectra in Fig. 1a. The most prominent band for all exhaust particles is the band of aliphatic C—H stretch vibrations of alkyl groups in alkanes, representing a functional group marker of hydrophobic surface chemistry. Strong asymmetric and symmetric stretches of methylene (CH_2) groups

are observed at 2924 and 2850 cm^{-1} , respectively. An asymmetric stretch of methyl (CH_3) groups is present at 2951 cm^{-1} as a weak shoulder of the stronger CH_2 asymmetric stretch. DSB1 operation was different from DSB2 by twice the revolution (Table 1), leading to a prominent band of carbonyl C=O stretch vibrations in carboxylic acids, ketones, aldehydes, esters, and lactones in the range of 1701–1776 cm^{-1} . A difference in revolution value and break mean effective pressure (BMEP) of operation DSB4 condition resulted in the most intensive band in the range 3200–3600 cm^{-1} , assigned to O—H groups in alcohols and phenols.

Fig. 1b shows IR spectra of diesel and rapeseed oil particles in exhaust of the John Deere engine operated under the stationary (DSJ-2, RSJ-4) and transient (RTJ-7, DTJ-8) conditions. Aliphatic C—H stretch vibrations and polyaromatic C=C—H bend vibrations are the most prominent features for all conditions. While PAH emissions from conventional diesel combustion are characteristically high, in this study only selected species in certain samples were observed above the analytical detection limit. Only naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene were detected. Mainly, three PAHs, i.e., phenanthrene, fluoranthene, and pyrene, were found at levels around 1% of PM mass in RTJ-7 and DTJ-8 exhaust. The impact of rapeseed oil as a fuel on the particle surface chemistry is indicated by C=O carbonyl (1705–1776 cm^{-1}) groups in oxygenated compounds. This finding is in good agreement with recent observations of functionalities of biofuel particles emitted by an Opel Astra diesel engine [23,31].

Water-soluble organic carbon (WSOC) in least polluting (DSB3) exhaust is comparable to DSJ-2 exhaust, while it is negligible in the most polluting (DSB4) exhaust (Fig. 2). Since WSOC is almost entirely composed of oxygen-containing compounds, the carbonyl functionalities observed for rapeseed oil exhaust (Fig. 1), determine the chemistry of WSOC. Examination of the WSOC fraction in PM (Fig. 2) proves the elevated concentrations of oxygen-containing compounds in particles produced by rapeseed oil combustion.

Individual particle analysis revealed the microstructure of the engine exhaust. Particle groups and their abundances for the most and least polluting conditions from the BMW engine stationary operation are shown in Table 3. Seven out of eight groups for least polluting (DSB3) exhaust present carbonaceous particles containing C as the dominant element. Soot type groups demonstrate the typical morphological features of soot chain agglomerates in primary particles with diameters ranging from 20 to 50 nm. These particles are separated between Group Typical soot, Elemental Carbon and Oxidized soot according to the oxygen abundance. The most abundant group in polluting exhaust is the Group Typical soot (38.1%), with a composition that is typical for hydrocarbon-produced soot [30]. These particles contain 93 wt% of C and 7 wt% of O, probably in oxygen-containing functionalities

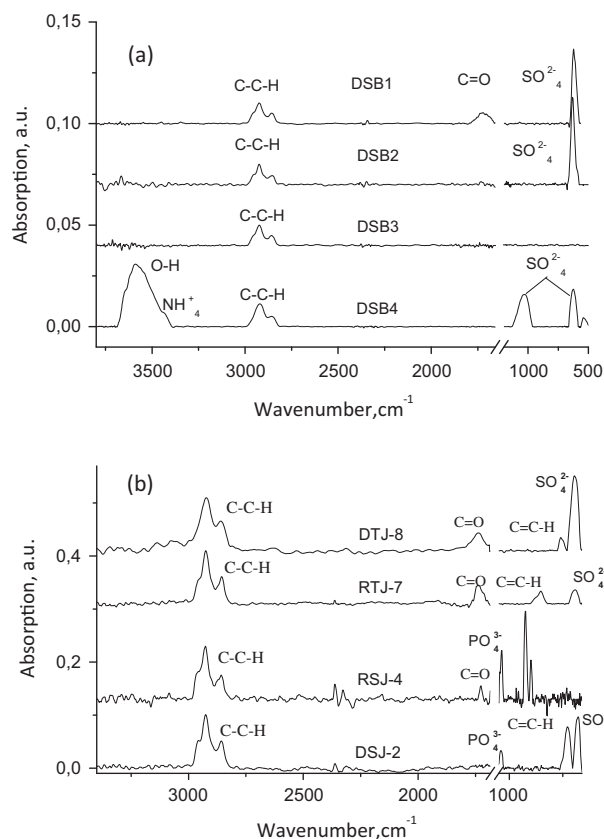


Fig. 1. FTIR spectra of exhaust particles produced by (a) BMW engine using diesel fuel in the most (DSB1, 2, 4) and least polluting (DSB3) stationary conditions, and (b) John Deere engine using diesel/rapeseed oil at stationary (DSJ-2, RSJ-4) and transient (RTJ-7, DTJ-8) conditions.

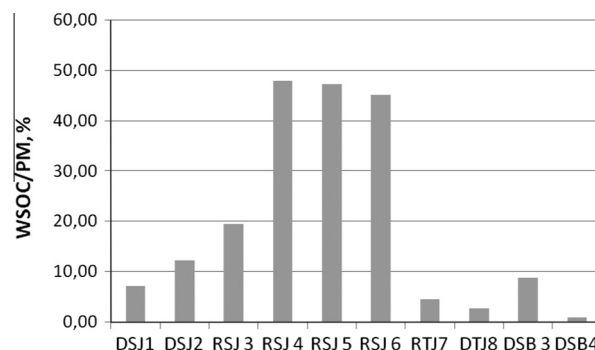


Fig. 2. Water-soluble organic carbon fraction in exhaust PM from the John Deere and BMW engines. Operation conditions are indicated in Tables 1 and 2.

Table 3
Groups of particles, average composition, and abundance in diesel exhaust of BMW engine under the most (DSB4) and least polluting (DSB3) conditions, and in diesel/biofuel exhaust from the John Deere engine under transient RTJ-7 and DTJ-8 conditions.

Groups	DSB3	DSB4	RTJ-7	DTJ-8
Typical soot	C ₉₃ O ₇ (38.1) ^b	C ₉₈ O ₂ (45.8)	C ₉₇ O ₃ (55.1)	C ₉₇ O ₃ (24.2)
Elemental carbon	C ₁₀₀ (12.5)	C ₁₀₀ (14.9)	C ₁₀₀ (24.2)	C ₁₀₀ (7.6)
Oxidized soot	C ₆₆ O ₃₂ (14.3)	C ₈₀ O ₂₀ (19.8)	C ₈₄ O ₁₆ (14.8)	C ₇₉ O ₁₉ (35.8)
Ca-rich	C ₅₆ O ₂₆ Ca ₁₁ S ₃ (5.2)	C ₆₆ O ₂₂ Ca ₉ (9.9)	C ₈₄ O ₁₃ Ca ₂ (1.9)	C ₆₀ O ₂₀ Ca ₁₀ (10.6)
Si-rich	C ₃₆ O ₃₇ Si ₂₃ Al ₂ (7.4)	C ₃₅ O ₃₀ Si ₂₉ Ca ₂ (4.2)	C ₅₆ O ₂₇ Si ₆ (1.9)	C ₂₅ O ₄₂ Al ₅ Si ₂₂ K ₄ (2.3)
S-rich	C ₈₀ O ₁₁ S ₈ (3.5)	C ₆₆ O ₂₂ S ₉ (1.9)		C ₆₄ O ₁₀ S ₂₅ (13.6)
Fe-rich	C ₄₆ Fe ₃₁ O ₁₇ (3.5)	C ₁₀ O ₄₁ Fe ₁₅ Mg ₄ Al ₁₁ Si ₁₄ K ₃ (1.1)	C ₇₄ O ₁₁ Fe ₄ P ₃ Al ₃ Ti ₃ (5.2)	C ₄₉ O ₁₅ Fe ₁₅ Al ₇ Ti ₈ Sr ₆ Sn ₂ (4.5)
Al-rich	Al ₄₉ O ₄₄ C ₆ (15.6)	C ₄₆ Al ₉ Si ₉ O ₂₇ K ₂ (2.3)		C ₄₉ Al ₁₃ O ₃₅ Ca ₃ (1.5)

^a Average group composition (wt%), elements with wt > 1% are indicated.

^b Group abundance (%) is indicated in brackets.

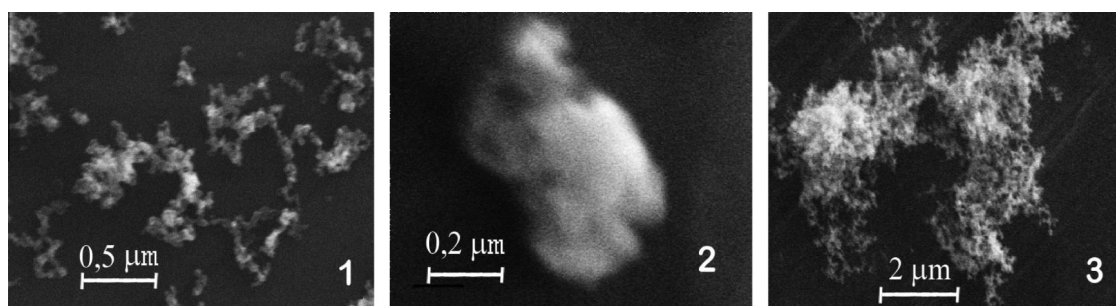


Fig. 3. Representative micrographs of Group (1) Typical soot (DSB4), (2) oxidized soot (RTJ-7), and (3) elemental carbon (DTJ-8) in the respective exhaust particles.

of organic compounds on the surface, as described above. Fig. 3a shows the micrograph of typical soot agglomerates in Group Typical soot. Group Elemental carbon is composed of 100% C. It was found previously in the microstructure of laboratory-produced hydrocarbon soot [30] and in the emissions of flaming burns of pine wood [31], being a characteristic feature of high-temperature combustion. The concentration of O in Group Oxidized soot approaches 20 wt%, probably due to a high amount of associated WSOC compounds. The microstructure of the most polluting (DSB4) exhaust indicates a higher abundance of each soot type group, in good agreement with the higher soot concentrations measured when the fouling of the exhaust cooler was pronounced.

The microstructure of diesel exhaust from the John Deere engine under DTJ-8 transient conditions showed around twice the abundance of the Group Oxidized soot compared to stationary DSB conditions (Table 3). In contrast, for rapeseed oil RTJ-7 exhaust, Group Typical soot and Elemental Carbon were dominant, while all soot type groups comprised as much as 94.1% of the entire exhaust, constituting the highest abundance of all soot particles observed in the studied emissions, mainly because of the low levels of inorganic impurities in biofuel compared with conventional diesel. The morphology of roughly spherical oxidized soot particles indicates the loss of the typical feature of soot chain morphology due to high amounts of organics on their surface (Fig. 3b), while the elemental carbon particles released during the DTJ-8 transient conditions demonstrate similar morphology to particles in diesel stationary exhaust (Fig. 3c).

3.2. Inorganic composition and fly ash microstructure

Diesel/biofuel exhaust particles are typically composed of C and O as the major elements and trace elements such as Si, S, Ca, Al, K, Fe, Ni, Cu, Sb, and P, contained in the fuel itself and in lubrication oil. The highest concentrations in bulk elemental composition of BMW engine exhaust are found for Si, Zn, and Ca, varying in the

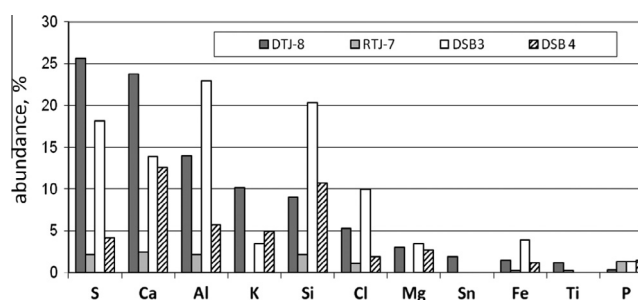


Fig. 4. Abundance of trace elements in individual exhaust particles from the BMW engine, using diesel fuel at the most (DSB4) and least polluting (DSB3) stationary conditions, and from the John Deere engine, using diesel/rapeseed oil at transient (RTJ-7 and RTJ-8) conditions.

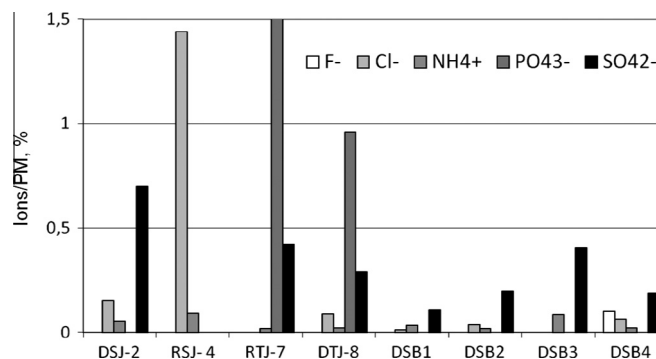


Fig. 5. Ion fractions in exhaust PM from John Deere and BMW engines. Operation conditions are indicated in Tables 1 and 2.

range from 5% to 67%, 3% to 31%, and 1% to 28% of PM mass, respectively, for different operation conditions. Other groups of individual particles observed in engine exhaust, different from soot types, are Groups Ca, Si, S, Fe, Al-rich (Table 3), where Ca, Si, S,

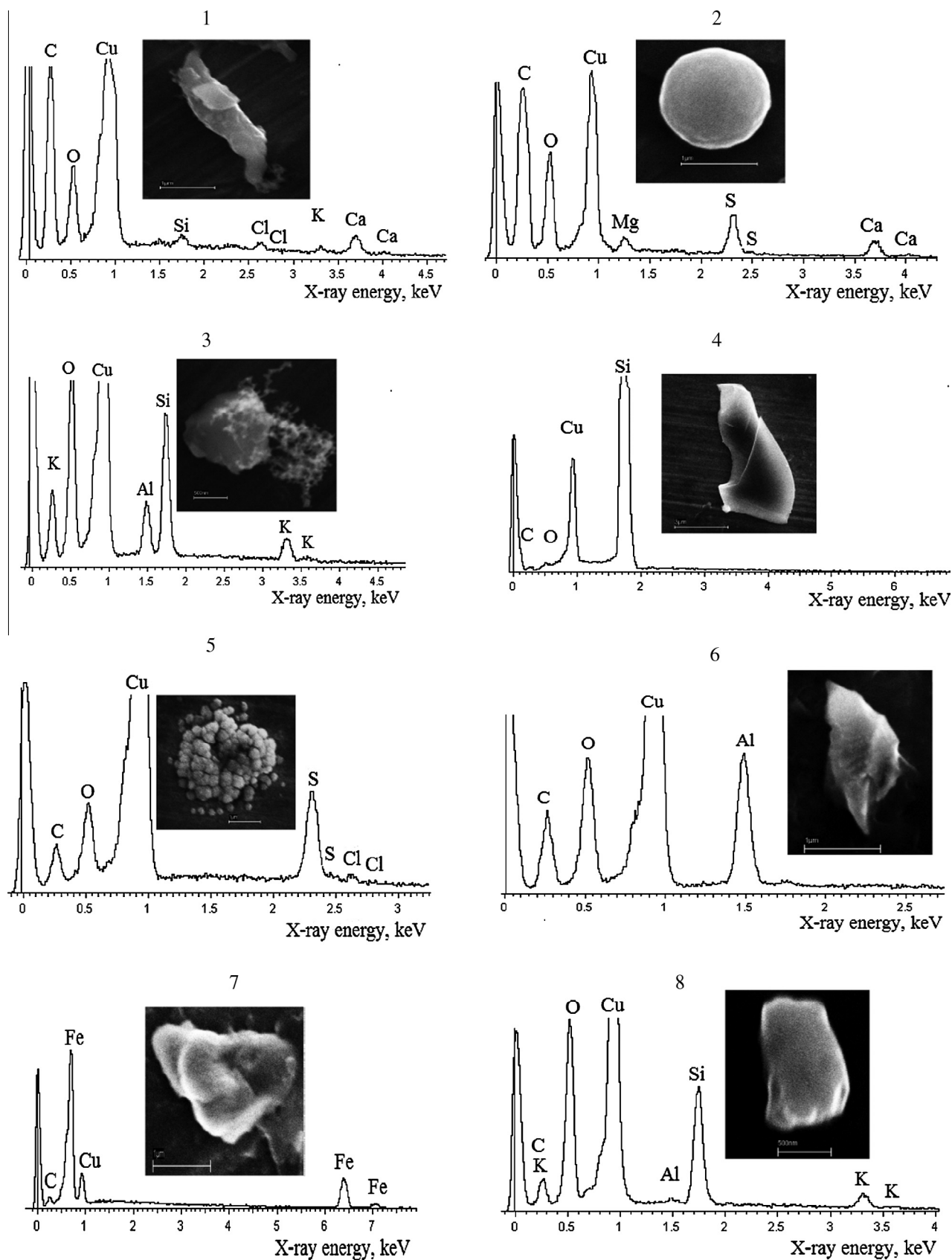


Fig. 6. Representative EDX spectra and micrographs of exhaust particles from BMW engine stationary operation. (1) CaO and (2) calcium sulfates (CaSO_4) in Group Ca-rich, (3) aluminosilicates (on left) and (4) quartz in Group Si-rich, (5) sulfuric acid in Group S-rich, (6) AlO in Al-bearing particles in Group Al-rich, (7) iron oxide in Group Fe-rich particles, (8) aluminosilicates accompanied by K in Group Al-rich. Cu is a substrate artifact.

Fe, Al elements are dominant after C and O, comprising fly ash, internally/externally mixed with the carbonaceous matrix. These groups contain irregular shaped particles in the size range >200 nm, which are formed during decomposition of fuel and lubrication oil, and subsequent oxidation and nucleation. The formation of coarse particles (>1 μm) can be explained by coalescence of molten grains of minerals during combustion while that of sub-micron particles occurs by vaporization–condensation mechanism.

Separation of individual particles into groups correlates well with the abundance of major trace elements. Fig. 4 shows Ca, Si, Al, and S as the most frequently distributed elements, other than C and O, at the most (DSB-4) and least (DSB3) polluting conditions of the BMW engine stationary operation. A full range of inorganic chemical species associated with water-soluble ions is shown in Fig. 5, supporting the identified types of particles mentioned above. In DSB4 exhaust around half of the particles in Group Ca-rich contain Ca probably in form of calcium oxides and/or calcium carbonates. A typical micrograph and EDX spectrum for particles from this group is shown in Fig. 6(1). Calcium sulfate can be identified in the other half of this group (Fig. 6(2)), in accordance with the high concentration of SO_4^{2-} ions shown in Fig. 5. Additionally, vibrations of sulfates are identified at 623 cm^{-1} in IR spectra for the most polluting conditions (Fig. 2a). They may be associated with ammonium sulfates because other characteristic bands of SO_4^{2-} and NH_4^+ ions are identified at 1043 cm^{-1} and in the range $3200\text{--}3600\text{ cm}^{-1}$, respectively. The NH_4^+ and SO_4^{2-} ion mass fractions in PM show large variability in the range of 0.02–0.28 wt%, and 0.01–0.2 wt%, respectively (Fig. 5). The highest wt% of sulfates is observed for low BMEP (1.61 bar) and low revolutions (830–1500 rpm).

Irregularly shaped aluminosilicates and quartz are found in Group Si-rich of BMW engine exhaust (Fig. 6(3) and (4)). Group S-rich with specific grain shape indicates that the soot agglomerate microstructure was modified by sulfuric acid condensation in the exhaust system (Fig. 6(5)), supported by the large O content and absence of cations which may produce inorganic sulfates. The dominant presence of Al and O as well as the typical crystallized shape of particles indicate aluminum oxides in Group Al-rich (Fig. 6(6)). As the engine bearings, heat exchangers, and engine block are made from Al, aluminum oxide could be a product of mechanical abrasion. According to higher lambda (3.46) for DSB3 vs lower value (1.37) for DSB4 conditions, the higher concentration of O in the first case apparently leads to the enhanced oxide formation under the less polluting conditions. Group Fe-rich is probably composed mainly of iron oxides (Fig. 6(7)). Moreover, aluminosilicates enriched by K are found in Group Al-rich (Fig. 6(8)).

Individual particle analysis performed for John Deere engine exhaust revealed the highest abundance of S and Ca elements at transient diesel (DTJ-8) conditions and lowest abundance of all elements in biofuel RTJ-7 exhaust, in comparison to diesel stationary BMW operation conditions (Fig. 4). Significantly higher content of sulfur in conventional diesel fuel DIN EN 590 than in rapeseed oil explains the low content (0.6 wt%) of SO_4^{2-} ions found under the stationary operation condition for diesel DSB-2 and the absence of sulfates for biofuel RSJ-4 exhaust (Fig. 5), which is in good correlation with the lack of sulfate vibrations in the IR spectra of rapeseed oil particles (Fig. 2). The SO_4^{2-} band is present in IR spectra from transient conditions, in accordance with the measured ions, but its intensity is significantly less in DTJ-8 than RTJ-7 exhaust. Very low sulfur content in rapeseed fuel, 35 times less than in conventional diesel, leads to absence of Group S-rich in RTJ-7 exhaust.

3.3. Hygroscopicity

Evidence that soot aerosols may be incorporated into cloud droplets, as they act as CCN, has been associated with

oxygen-containing active surface functionalities [18] and the presence of water-soluble fractions of organic and inorganic chemical species [32]. Higher concentrations of WSOC and SO_4^{2-} ions under least DSB3 compared to the most polluting (DSB4) conditions of diesel stationary BMW operation allows the general conclusion of the higher extent of hygroscopicity of exhaust particles in the first case. Probably, the operation conditions under higher combustion air ratios (lambda), leading to the higher concentration of oxygen (Table 1), are mostly responsible for the soot particle hygroscopicity.

For quantification of water uptake, the individual particles are separated into three fractions of different elemental composition, according to the method of Kireeva et al. [21]. Particles of soot type groups identified by cluster analysis belong to the C–O fraction. Group S- and Ca-rich comprise the C–O–S–Ca fraction. The remaining groups of Si- and Fe-rich particles impact the fraction C–O–Si–Fe of typical mineral content. The proportions of particles in the different fractions of DSB3 and DSB4 exhausts are shown in Fig. 7.

Reference diesel fuel flame soot with $\text{O/C} \leq 7\%$ provides the criterion for hydrophobic (PHO) particles of the C–O fraction [21]. Examination of the O/C ratio in the C–O fraction of diesel stationary exhaust shows the concentration of PHO particles being more than twice of those in DSB4 compared to DSB3 exhaust (Table 4), in good agreement with the higher EC and lower oxygen content in typical and oxidized soot (Table 3). Higher concentrations of hydrophilic (PHI) soot with $7\% < \text{O/C} \approx 12\%$ and hygroscopic (SCOP) particles with $\text{O/C} > 12\%$ are found for the less polluting conditions (Table 4), supported by larger WSOC content in DSB-32 exhaust (Fig. 3).

The second C–O–S–Ca fraction is composed of particles with the trace elements S, Ca, Cl, and K. As only the NH_4^+ cation is found in the water-soluble fraction, (Fig. 5), we assume the presence of sulfates in form of sulfuric acid and/or ammonium sulfates, which may change the particle hygroscopicity more significantly than water-soluble organic compounds [33]. The O/C ratio in the C–O–S–Ca fraction is found to be higher than in the C–O fraction. Diesel fuel flame soot covered by H_2SO_4 shows $\sim 1.3\text{ wt\%}$ of S can

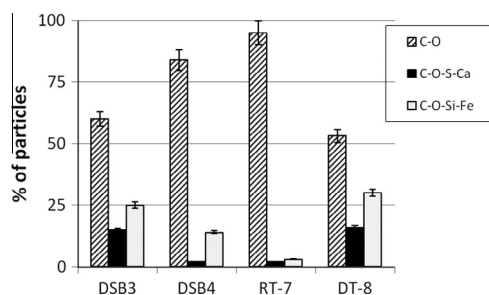


Fig. 7. Fractions of C–O, C–O–S–Ca, and C–O–Si–Fe in DSB3, DSB4, RTJ-7, and DTJ-8 exhaust samples.

Table 4

Categories of hydrophobic (PHO), hydrophilic (PHI), and hygroscopic (SCOP) fractions, in %, in C–O and C–O–S–Ca functionalities in diesel exhaust from the BMW engine under the most (DSB4) and least polluting (DSB3) conditions, and in diesel/biofuel exhaust from the John Deere engine under transient RTJ-7 and DTJ-8 conditions.

Fractions	C–O			C–O–S–Ca		
	PHO	PHI	SCOP	PHO	PHI	SCOP
DSB3	54	17	29	0	2	98
DSB4	68	10	22	0	0	100
RTJ-7	84.7	7.0	8.2	14.3	0	85.7
DTJ-8	58.2	7.8	34.0	9.1	4.5	86.4

change the hydrophobic properties of the surface to hydrophilic character, while 3 wt% of S transforms them into hygroscopic particles [21]. This criterion provides only 2% of PHI particles in the C—O—S—Ca fraction at less polluted condition, others are SCOP ones, and 100% of particles are SCOP under the most polluting conditions of diesel stationary BMW operation.

The proportions of particles in different fractions as well as categories of PHO, PHI, and SCOP particles in RTJ-7 vs DTJ-8 exhaust for the transient John Deere engine operation are shown in Fig. 7 and Table 4, respectively. In the fraction C—O, biofuel produces the highest proportion of PHO particles compared with conventional diesel, while SCOP particles are predominant in diesel exhaust. The highest percentage (around 86%) in the C—O—S—Ca fraction in both RTJ-7 and DTJ-8 exhaust are SCOP particles, in good agreement with high SO_4^{2-} ion content (Fig. 5).

4. Conclusions

Combining microanalysis of individual particles and bulk chemical characterization provides comprehensive morphological, elemental, chemical, and hygroscopic information for diesel/biofuel particulate exhaust from modern internal combustion engines, operated under stationary and transient non-road driving conditions. Examination of the emitted particles reveals the exhaust microstructure in terms of soot and fly ash particle groups, thus improving the characterization of aerosols for transport emission inventories. Under the most polluting conditions with respect to fouling of the exhaust system the conventional diesel exhaust microstructure indicates a higher abundance of soot type groups. Rapeseed oil particles are mostly comprised of soot type groups because of low impurity contents of biofuel and lubricating oil. Comparison analyses with recent findings from engine emission studies shows that the changes in fuel and design of diesel engines do not change the multicomponent character of engine particulate emissions and heterogeneous distribution of compounds at the microscopic level, which is impacted by both fuel and lube oil content and operation conditions.

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