Microstructure and Chemical Composition of Diesel and Biodiesel Particle Exhaust

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ABSTRACT

The complexity and large variability of transport-emitted aerosols leads to necessity of comprehensive characterization of their physico-chemical and toxicological properties, remaining great uncertainties in health effect assessments. Particles produced by combustion of fossil diesel (B0), 20% rapeseed methyl ester in fossil diesel (B20), and pure rapeseed methyl ester (B100) were sampled from exhaust of an Opel Astra diesel engine using sulfated ash, phosphorous and sulfur (SAPS) lube oil with low and high ash content. Microscopic and chemical characterization is performed to quantify the common and specific properties of diesel/biodiesel exhausts. Hydrophobic saturated aliphatic dominate diesel particle chemistry. Oxygen and nitrogen-containing functionalities are specific for more hydrophilic biodiesel particles. A full range of chemical species for individual particles is grouped by clustering technique combined with water-soluble ion measurements. Analysis of group abundance shows carbonaceous particles (soot externally mixed with inorganic salts) and inorganic fly ash (metal oxides) in a structure of exhaust, in correlation with inorganic contaminations in fuel and lube oil. Quantification of particle types in terms of physicochemical relevance supports the identification of groups which may act as biomarkers discriminating between diesel and biofuel exhaust and micromarkers of using high ash lube oil, thus providing a basis for correlative toxicological assessment of diesel/biofuel engine emissions.

Keywords: Combustion particles; Diesel exhaust; Aerosols.

INTRODUCTION

Combustion aerosols are the ubiquitous substance that is produced by incomplete burning of fossil fuels and biomass. Transport activities contribute 20–25% of total anthropogenic emission of carbonaceous particles (Cofala et al., 2007). In Europe more than 70% of carbonaceous aerosols originate from the transport sector. The composition of combustion aerosols significantly impacts air quality, radiative balance, and climate (Chow and Watson, 2011). Investigations of their physico-chemical properties are gaining importance due to enhancement of air pollution reduction relating to improvement of engine performance, fuel efficiency, and after-treatment strategies.

Currently diesel exhaust particles are gaining an increasing attention because of pronounced impacts on human health (Donaldson et al., 2005). They are considered as dangerous pollutants because of high number density, small respirable size, large surface area, and potential toxicity. Particle toxic potential has been associated with serious adverse health effects, including respiratory symptoms impaired lung function and cardiovascular diseases (Geller et al., 2006; Bernstein et al., 2004). It is found that newer diesel engines emit nanoparticles that could be more harmful to human health than older engines because particles with diameters of 5–20 nm may penetrate the lung more deeply (Su et al., 2008).

Diesel soot emitted by modern engines demonstrates defective surfaces with chemically reactive sites which destabilizes the carbon structure and may increase soot cytotoxicity. InfraRed studies show a high concentration of hydroxyl functional groups on Euro IV soot compared to soot emitted by older engines (Su et al., 2008), and hence an increased hydrophilicity which facilitates interactions...
with hydrophilic biomolecules (Popovicheva et al., 2009a). Based on inflammatory and cytotoxic responses to in vitro and in vivo particle exposures, the hazardous substances are found on particles emitted by various vehicles but risks associated to chemical forms of these emissions are remaining uncertain (Maiert et al., 2008; Muller et al., 2010). Due to a lack of characterization data the current practice for assessing effects of diesel-produced particles on air quality is based largely on the quantity of emitted particles and their size, and limited on their chemical composition and toxicological properties.

Since the particle formation depends on several factors, e.g., type of fuel and engine operation conditions, their morphology and composition varies considerably. Carbonaceous components of fossil fuel-derived particulate matter contain ultrafine soot agglomerates with fractal chain morphology and spherical primary particles between 30 and 50 nm in diameter (Chen et al., 2005). A basic feature of soot is the elemental carbon microstructure of graphite microcrystallites (Popovicheva et al., 2003; Vander Wal et al., 2007). Unburned organic components and inorganic contaminations in fuel, lube oil, and engine wear are condensed on soot particles in chemical forms of organic carbon (OC) and inorganic fly ash that together comprise extremely complex exhaust structure (Kleeman et al., 2000; Sakurai et al., 2003; Toner et al., 2006). The OC content varies with engine operating conditions and can represent 5–90% of total particulate mass dominated by alkanes, hopanes, steranes, and polyaromatics (Chow et al., 2007). Single particle characterization of heavy duty diesel emission demonstrates that particles made from elemental carbon (EC), OC, Ca, and phosphates are dominating (Toner et al., 2006). The increase of engine speed results in increased metal content of crustal origin (Wang et al., 2003). All conventional piston-driven combustion engines emit metal oxide particles produced in nucleation processes during combustion due to abrasion, catalyst coatings, metal-organic lube oil and fuel additives (Mayer et al., 2010).

Fatty acid methyl esters (FAMEs), also referred as biodiesel, are oxygenated fuels made from vegetable oils and animal fats via transesterification. They have long been recognized as reducing the exhaust particle mass and number as compared to diesel fuel (Jung et al., 2006; Betha and Balasubramanian, 2011). The increase in consumption of biodiesel blend fuels led to changes in diesel pollutant emission (Singh and Singh, 2012) including changes of physico-chemical properties of the emitted particles, their size (Jung et al., 2006), the soluble organic fraction (Dwivedi et al., 2006), and metal content (Dwivedi et al., 2006; Betha and Balasubramanian, 2011). Health risk estimates based on exposure and dose-response assessments of particulate-bound elements revealed that biofuel exhaust is more hazardous (Betha and Balasubramanian, 2011).

There are strong indications of particle biological activity in dependence on physico-chemical characteristics, which are not considered in many toxicity studies (Oberdorster et al., 2005). Risk assessment of diesel exhaust emissions was done by exposing the exhaust directly to the surface of lung cells cultured at the air-liquid interface (Steiner et al., 2012). A complex three dimensional cellular model of the human lung epithelium was used to present the lung cells (Rothen-Rutishauser et al., 2008; Muller et al., 2010). Volatile and soluble organics content are found to be higher in biodiesel exhaust compared to standard diesel (Dwivedi et al., 2006). Diesel particles contain substantially more PAHs than rapeseed oil while carcinogenic PAH level is higher for rapeseed oil exhaust (Topinka et al., 2012).

The effects of inhaled aerosols at the cellular level depend on both their size and distribution of toxic components over particles. Most diesel exhaust studies have aimed to obtain the information on average chemical characteristics by bulk analytic techniques while characterization of individual particles is significant for health impact assessment as providing the chemical composition and morphological information at the microscopic level. Single particle analysis reveals the particle types to present the major signatures in exhaust (Toner et al., 2006). Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray Spectroscopy (EDX) is a powerful tool for characterization of size, morphology, and composition of individual particles in combustion emissions (Chen et al., 2005, 2006; Vester et al., 2007; Kireeva et al., 2009).

Characterization of multicomponent diesel exhaust previously was done in accordance with morphological specification, such as soot-like, char, and mineral particles (Chen et al., 2005; Popovicheva et al., 2009b). However, cluster analysis is presently well-developed multivariate data analysis technique useful for interpretation of electron microprobe analysis data (Popovicheva et al., 2012). The range of similar species in exhaust may be grouped revealing the particle types according to morphology and composition. With this purpose bulk analytic techniques are useful to identify inorganic compounds and ions in the diesel engine exhaust.

This paper is devoted to characterization of microstructure and chemical composition of particle exhaust produced by Opel Astra X20DTL engine using diesel and biodiesel, and lube oil of different purity (low and high SAPS). The individual particle analysis is performed by SEM/EDX to determine the morphology and composition of aerosols produced at controlled combustion conditions. For classification of individual particles and quantification of structure of the exhaust the cluster analysis is performed. Expert analysis based on water-soluble inorganic ion measurements is applied for interpretation of clustering data and best separation on characteristic groups. Micrometer of using high SAPS lube oil and biomicrometer of biodiesel using are identified. Results of characterization are discussed together with toxicological responses of human lung cells exposed by B0, B20 and B100 exhaust at the air liquid interface, including cell death, induction of oxidative stress, and pro-inflammatory responses.

**EXPERIMENTAL**

An Opel Astra X20DTL was running on a dynamometer at a constant velocity of 35 km/hr with a force of 66N at the wheel. The test vehicle was a 4 cylinder Diesel engine, 1994 cc displacement, production year 1998 and 70000 km...
mileage. This vehicle was little used and at normal technical state without excessive oil consumption. Conventional diesel fuel DIN EN 590 (B0) of swiss market quality, a blend of 80% fossil diesel and 20% rapseed methyl ester (B20), and pure fatty rapseed methyl ester (B100) were used as fuels. Sulfur content in B0 and B100 is 10 and 5.2 mg/kg. Ca, K of 5.6 and 3.4 mg/kg are found in B100. V10.237 and V10.240 sulfated ash, phosphorous and sulfur (SAPS) contained high and low ash of 1.5 wt% and <0.7 wt%, respectively, were used as lube oil. Composition of ash is dominated by Ca, S, and Zn content.

Sampling of total suspension particles was performed with a CVS system at B0 low and high SAPS, B20 high SAPS, and B100 high SAPS conditions. For particle sampling fluorocarbon-coated borosilicate glass fiber filters (T60A20, Pall Life Sciences) were used. Sampling was repeated three times for each from four conditions to estimate the combustion variability impact on particle properties.

The particle chemical composition was analyzed by Fourier Transform Infrared (FTIR) spectroscopy using a Shimadzu IRPrestige-21 spectrometer in a transmission mode. FTIR spectra are measured at 4 cm⁻¹ resolution. Each spectrum was an average of 100 scans in the typical wavenumber range from 4000 to 500 cm⁻¹. Irisolution (Shimadzu) software was used to subtract the spectrum of a blank filter from the spectrum of the loaded filter, and to correct the baseline absorbance. The scaled subtraction was performed by the spectrum normalization on a band at 1400 cm⁻¹. The difficulty in completely subtracting out the strong blank filter absorption in the region of 1200–800 cm⁻¹ reduces the usefulness of analysis in this region. Moreover, the spectra of sample filters do not demonstrate any absorbance bands in the region of 800–450 cm⁻¹. This is why all following spectra interpretation is done in the region of 3600–1250 cm⁻¹. Identification of absorption bands is carried out according to a FTIR database (Lin-Vien et al., 1991; Coates, 2000) and measurements of standard compounds.

Water-soluble inorganic ion mass concentrations were measured using a capillary electrophoresis (CE) system (Capel-103, Lumex Corp.). Six anions (SO₄²⁻, NO₃⁻, Cl⁻, F⁻, NO₂⁻, and PO₄³⁻) and six cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Sr⁺, and Ca²⁺) were determined in aqueous extracts. One-forth filter sample was extracted in 5 ml of distilled water by ultrasonic agitation for 30 min, and then the extract was filtered. CE methodic details are described elsewhere (Kaniantsky et al., 1999). Because large contaminations of blank filters T60A20 by NH₄⁺, Na⁺, K⁺, Cl⁻ the measurement error (std) for these ions were high, in the range from 39 to 66%. For other ions SO₄²⁻, Ca²⁺, Ba⁺, Cl⁻, NO₃⁻ it was 49, 50, 39, 46, 34%, respectively.

Individual particles were examined using the LEO 1430-vp (Karl Zeiss) field emission scanning electron microscope with a spatial resolution of 7 nm equipped with an Oxford energy dispersive detector INCA. Energy dispersive X-ray spectroscopy spectra for Z elements (Z ≥ 5) were recorded in SEM image mode and then quantified by means of a method that relates the measured X-ray intensity to the elemental concentration, using calculated equivalent X-ray intensities of corresponding elements. Counting time for X-ray spectra was 50 seconds at 5.9 kV. Particles from the sample filters were removed onto Cu substrate by ultrasonic treatment during 30 min. Approximately 500 fine individual particles with a diameter from 0.1 up to 3 μm were chosen for each sample, a number sufficient to get certain types of particles in the each sample (Chen et al., 2006; Popovicheva et al., 2012). Significantly larger sizes were not considered because relating to coarse agglomerates. Small concentrations of C and O in the substrate were subtracted from the EDX spectra of analyzed particles.

The result of EDX analysis was a data matrix of 20 element weight concentrations. Combination of hierarchical and non-hierarchical cluster analysis, k-means and g-means, was applied to separate individual particles in definable groups of similar chemical composition using software Deductor. More details are described elsewhere (Bladt et al., 2012; Popovicheva et al., 2012). The justification for the number of groups of the best separation is the identification of different chemical particle types. In this case the clustering with lower number of groups does not provide a good separation while a higher number leads only to duplication of groups with similar composition.

RESULTS AND DISCUSSION

Chemical Composition

FTIR analysis gives a good overview of exhaust particle chemical composition. Fig. 1 shows representative FTIR spectra of particles produced at B0 low and high SAPS, B20 high SAPS, and B100 high SAPS conditions. The observation of high similarity for FTIR spectra of samples repeatedly produced at the same condition reveals a high reproducibility of engine operation. The most intensive spectral feature for all emissions is bands of aliphatic C=C-H stretch vibrations of alkyl groups in alkanes. Strong asymmetric and symmetric stretches of methylene CH₂ groups are observed at 2924 and 2853 cm⁻¹, respectively. An asymmetric stretch of methyl CH₃ groups is slightly prominent at 2951 cm⁻¹ as a weak shoulder of a much stronger CH₂ asymmetric stretch. The bands at 1456 and 1375 cm⁻¹ are assigned to asymmetric and symmetric bend vibrations of methyl alkyl groups. There is a difference in composition between low and high SAPS for any fuel used due to a wide band in the region of 1517–1533 cm⁻¹ associated to aromatic -NO₂ vibrations but for diesel fuel it is very slightly prominent.

The band of carbonyl C=O stretch vibrations in the range of 1718–1753 cm⁻¹ is related to carboxylic acids, ketones, aldehydes, esters, and lactones. It is the most significant for B100 high SAPS than for B20 high SAPS, relating to higher carbonyl production in biofuel exhaust (Karavalakis et al, 2011). As a peak area of FTIR band is assigned to abundance of functionalities, a higher ratio of carbonyl C=O to aliphatic C-C-H band indicates more hydrophilic character of the surface for B100 than for B20 particles.

In the region of 580–680 cm⁻¹ relatively significant vibrations of SO₄²⁻ ions are indentified, they are produced due to sulfur contaminations either in fuel or oil. While...
slightly prominent $\text{NO}_3^-$ ion vibrations are observed at 833 cm$^{-1}$ for B0 high SAPS, they are more significant for B20 and B100 high SAPS, relating to higher nitrification of the particle surface in the biofuel exhaust. Also, in last case the band in the region of 1357–1365 cm$^{-1}$ is associated to $\text{NO}_3^-$ vibrations.

Mass concentrations of water-soluble inorganic ions in diesel and biodiesel exhaust particles are shown in Fig. 2. $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{NO}_3^-$, $\text{K}^+$, $\text{Ba}^+$, and $\text{Cl}^-$ ions account for more abundant ionic species in all exhausts. $\text{NO}_3^-$ ions dominate at high SAPS for any fuel used, well in accordance with FTIR data, its maximum concentration approaches 1.0% of particulate mass. In comparison with low SAPS exhaust, higher concentrations of $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ions are observed at high SAPS, in accordance with elevated ash content in high SAPS. Variable concentrations of ammonium, potassium, sodium, calcium, and chloride as well as sulfates and nitrates ions indicate the presence of water-soluble salts in diesel/biodiesel particles.

**Individual Particle Analyses**

Individual particle analysis reveals the complex structure of aerosol exhaust produced by an Opel Astra engine. SEM/EDX observations show carbonaceous particles internally and externally mixed with inorganic compounds. The composition of individual particles is varying in a wide concentration range of common (C, O) and trace elements representative fuel and lube oil content. Groups of particles identified at B0 low and high SAPS, B20 high SAPS, and B100 high SAPS conditions and their abundances are presented in Table 1. Using the cluster analysis of the chemical composition combined with morphological information it is reasonable to propose the group identification according the chemical particle types.

Soot particles are formed via vaporization-condensation of fuel hydrocarbons during combustion. In accordance with specific features of soot they are typically observed for diesel emissions (Clague et al., 1999; Miller et al., 2007; Kireeva et al., 2009). Group Soot composes the major part
of carbonaceous particles in all exhausts; it consists of
chain agglomerates with morphology of primary roughly
spherical particles of diameter from 20 to 50 nm. In average,
soot contain mostly C and O with a negligible amount of
other impurities (<2 wt%). The agglomerate size ranges
from 100 nm to 1 µm.

In Group Ca, Si, and Na, Cl, K-rich these elements are
most abundant after carbon and compose fly ash internally/
externally mixed in carbonaceous matrix. Groups Fe-, Al-, Zn-, Nb-, W- bearing are identified according to the
content of major element higher than C which determines
the particle type. All these groups contain irregular shaped
particles in a size range > 200 nm. They are formed during
decomposition, subsequent oxidation, and nucleation of
contaminations in fuel and lube oil. The formation of coarse
particles (>1 µm) can be explained by coalescence of
molten grains of minerals in fuel during combustion while
that of submicrometer particles occurs by a vaporization-
condensation mechanism (Lighty, 2000). The abundance of
elements over individual particles, other than C and O, is
shown in Fig. 3. As seen, Ca, Si, Al, and Fe are the most
abundant for all emissions studied, and they compose the
separated groups.

For diesel B0 low SAPS the clustering of the particles
on five groups gives the best separation. For demonstration
of element variability the group average composition and
standard deviation are presented in Table 2. Representative
SEM micrographs of B0 low SAPS groups are shown in
Fig. 4. The most abundant is Group Soot composed from
well-fused primary soot particles. Particles of Group Si-
bearing are mostly quartz because the large amount of O
and angular chips shape found for SiO₂ particles formed
during combustion. However, small amount of Al
accompanies Si in one third fraction of particles in this
group, relating to various aluminum silicates. Group Fe-
rich is dominated by Fe and O associated with the irregular
shaped iron particles, observed in Miller et al. (2007).
They typically originate from engine wear and corrosion,
and presented by iron oxide (Bladt et al., 2012). Group Ca-
rich is probably a mixture of calcium carbonate (CaCO₃)
and calcium oxide (CaO). Some amount of S observed may
allow suggesting the presence of calcium sulfates, in
correlation with sulfates ions measured. Group Al-bearing
is composed of aluminum oxide because of large O content
and morphologically well-formed crystals.

Relating to elevated abundance of P, Al, W, Ni, Nb, Mg,
Zn, S, and Ti over particles at high SAPS, Fig. 3, we
conclude the impact of contaminations in lube oil on the
particle composition. Representative micrographs for groups
of diesel B0 high SAPS are shown in Fig. 4. Using lube oil
of high ash content leads to decreasing of Si and Fe oxide
particle groups for diesel B0 high SAPS while the most
prominent result is the appearance of Group Nb- and W-
bearing composed from niobium oxide and tungsten particles,
respectively. Thus, we may relate Groups Nb- and W-
bearing as micromarkers of using of high SAPS lube oil.

For biodiesel B20 exhaust structure the clustering
reveals the similar groups of soot externally mixed with
inorganic salts and metal oxides as for diesel one. However,
new specific Group Na, Cl, K-rich is found where marker elements of biofuel combustion Na, Cl, and K create the separate group and significantly contribute its overall composition. Representative micrographs for groups of B20 high SAPS are shown in Fig. 4. Abundance of Cl is significantly increased for biofuel emissions, Fig. 3. Because alkaline earth and alkali compounds are easily vaporized creating fumes under combustion conditions, at the exhaust cooling they may produce ultrafine particles externally mixed with others. Chlorine in these particles may exist in ion form, in accordance with ion measurements, Fig. 2, producing sodium and potassium chlorides. Group Zn- and W-bearing may also serve as micromarkers of high SAPS lube oil.

For biodiesel B100 when diesel fuel is completely replaced by biofuel we observe the group with K as dominant element at averaged concentration of 7 wt%. In accordance with well-recognized assignment of potassium to biomarker of biomass burning (Reid et al., 2005) we may propose Group Na, Cl, K-rich in biodiesel exhaust as biomarker of biodiesel using. Elevated abundance of S over particles in B100 high SAPS demonstrates the impact of high ash content in lube oil relating to sulfates production, thus indicating Group S-bearing as micromarker of high SAPS lube oil in this exhaust.

**Exhaust Toxicity**

In our recent study of Steiner et al. (2013) in framework of the same measurement campaign the Opel engine exhaust was diluted then folds with heated filtered ambient air to expose a complex 3D cellular model of the human airway epithelium in vitro at the air-liquid interface. In parallel to exhaust exposures, identical cell cultures were exposed to filtered ambient air, which allows differentiating between exposure system and cell culture effects from purely exhaust. The cell cultures were exposed for 2 or 6 hrs to exhaust samples or filtered air followed by a 6 hrs post-incubation. An assessment was performed by toxicity tests of exposed cells, i.e., cytoxicity, oxidative stress, and inflammation. Pro-inflammatory responses were assessed by quantification of the pro-inflammatory cytokines tumor necrosis factor TNF-α and interleukin IL-8 by enzyme linked immune-sorbent assay (ELISA). A detailed discussion of toxicological findings is given elsewhere (Steiner et al., 2013).

Here we perform the particle characterization study for the same engine operation conditions when cell exposure tests were done and no significant cytotoxic reactions found at different fuel and lube oil conditions. All exhausts induced considerable oxidative stress. The effect was weaker for B0 low SAPS in comparison with high SAPS. If particle properties in exhaust are the most important factor influencing the biological responses, we may relate micromarkers of contaminations in lube oil found for high SAPS exhaust to this effect because hydrophobic character of nonoxidized surface of diesel exhaust and undistinguishable difference in organic chemistry. Using pure fatty rapeseed methyl ester for B100 high SAPS leads to increasing the oxidative stress in comparison with B20 high SAPS, thus indicating the role of biofuel composition which may be associated with biomicromarkers found for biofuel exhausts as well with higher oxidation and nitrification of the biofuel particle surface, relating with higher reactivity and oxidation behavior.

Diesel/biodiesel exhausts are found capable of inducing pro-inflammatory responses, a finding dependent on the exposure duration and the pro-inflammatory marker under investigation. The highest induction of TNF gene expression is detected for B0 high SAPS (comparable for 2 and 6 hrs exposure), B100 high SAPS (6 hrs) and B0 low SAPS (6 hrs). Exposure to B20 high SAPS, B100 high SAPS (2 hours) and B0 low SAPS (2 hrs) exhaust did not induce TNF expression. A similar picture was obtained for IL-8 gene expression (which is the biological downstream event of TNF expression): highest induction for B0 high SAPS, B100 high SAPS (6 hrs) and B0 low SAPS (6 hrs). Transcriptional induction of IL-8 upon 2 hours of exposure to all tested exhaust types is lower than the one observed for B0 high SAPS and comparable to each other. In contrast to what is found for TNF gene expression, 6 hours exposure to B20 high SAPS clearly induce IL-8 expression, even though to a lower extent than B0 high SAPS, B100 high...
CONCLUSIONS

Microscopic and chemical characterization of multicomponent diesel/biodiesel exhaust particles allows the quantification of major physico-chemical properties relating with morphology, elemental composition, organic/inorganic content, and type of particles. The comprehensive analysis elucidates how combustion aerosols are changed in dependence on fuel and lube oil to reveal the general properties and distinguish the specific ones for diesel/biodiesel exhaust particles. Fuel additives, oil contaminations, and engine wear impact multicomponent aerosols composed of inorganic compounds (salts and metal oxides) emitted together with soot particles. Calcium, potassium, sodium combined with sulfates, chlorides, and nitrates compose inorganic salt compounds.

Chemical composition of diesel/biodiesel particles is dominated by aliphatic C-H groups in alkanes with relative low carbonyl C=O groups in carboxylic acids, ketones, aldehydes, esters, lactones, aromatic -NO₂ groups in nitrocompounds, and NO₃⁻ and SO₄²⁻ ions in inorganic salts. The relative concentration of carbonyl groups increases with the biodiesel fraction in the fuel, thus providing the increased surface hydrophilicity from hydrophobic for diesel B0 to the most hydrophilic for biodiesel B100. Hydrophilic character of nonoxidized surface of diesel exhaust is prominent and may determine the specific surface reactivity. More functionalized biodiesel particles may have a higher reactivity and show some oxidation behavior. The most developed functionalities are specific for biodiesel B100 particles with 100% of biofuel.

The diesel/biodiesel exhaust structure reveals the groups of carbonaceous and fly ash particles, in according the quantification of particle types in terms of physicochemical relevance. The most abundant group is typical soot agglomerates of mostly carbon and oxygen content at both diesel and biodiesel, low and high SAPS. Using high ash lube oil increases the abundance of metal (Nb, Zn, W) oxide and sulfur-containing groups while biodiesel fuel brings separate group with Na, K, and Cl biofuel markers. Thus, micromarkers discriminating between low and high ash-containing lube oil and the different types of fuels may be proposed. They could enable the classification of multicomponent aerosols according to diesel/biodiesel combustion source.

Individual particle analysis improves the characterization of multicomponent diesel/biodiesel particles for toxicological studies. The identification of morphological and...
compositional micromarkers in emissions from combustion of fossil fuel and biofuels help elucidating toxicological properties of diesel exhaust under different combustion conditions. However, not all cellular reactions can be explained by those parameters due to possible large impact of gaseous exhaust. How exactly morphology, elemental composition, and organic/inorganic composition of exhaust particles translate into biological effects is not understood in detail so far.

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