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Air particulate emission monitoring of diesel combustion products

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1. Introduction

Aerosols are receiving more attention with the onset of the nanotechnology era leading to a stronger critique of emissions and a surge of interest in the manufacture of functional nanoparticles. Both of these directions need reliable aerosol monitoring techniques, with a requirement to measure aerosol characteristics over a shorter time scale. A progress in aerosol measurement technology needs to provide faster sensing and a more thorough understanding of the aerosol characteristics. Providing aerosol sensors at affordable prices to the community will increase awareness of clean air conditions for the community. A better understanding of the measurement techniques and their capabilities will lead to easier implementation of aerosol sensors and will support the developments for greener manufacturing, cleaner office environments and improved climate conditions.

2. Rationale for measuring aerosols

2.1 The objective of the study is to assemble information on the effect of air particulate from diesel combustion processes, characterize the form of air particulate and investigate processes that could be used to monitor emissions from the shipping industry.

2.2 The target stakeholders include ports, the shipping personnel, and citizens from different countries that live in coastal cities adjacent to major shipping routes.

2.3 Climate, air quality and environment

Black carbon from automotive emissions, domestic fireplaces and industries impact the climate and add to the effect of CO_2 in global warming. This has a follow-on effect on the marine export production[2], a change in coral species in the oceans[3], faster melting of ice in the Arctic[4], in addition to the poor visibility and staining of buildings in heavily populated cities. The reduction of black carbon possibly provides the most effective method of slowing global warming. Eliminating all fossil fuel black carbon and organic matter could remove 20-45% of the net warming within 3-5 years, but reducing the CO_2 emissions by a third will have the same effect, but after 50-200 years.[5] Progress in this area requires fine particulate sensing and filtration equipment.

2.4 Health Industry

Airborne particulate will quickly impact the wellbeing of people, especially the elderly with pre-existing respiratory and cardiovascular diseases. Clinical studies have suggested a possible relationship between particulate air pollution and heart rate variability.[6] It has been suggested that fine particles can escape alveolar macrophage surveillance and move into the body undetected by the body's defence mechanisms.[7] Independent studies on polystyrene beads have shown accented lung inflammation with smaller particle size[8]. For other particle, the effect on health was initially attributed to the size, with smaller sizes being more harmful. Comparing materials, titanium oxide has shown to be more harmful than carbon black[9]. Although carbon nanotubes are roughly similar to carbon black, the more toxic nature could not be related to any specific factor such as the chemistry, structure, shape and size.[10] It has recently been shown that crystal structure plays an important role with anatase inducing cell necrosis, but rutile initiating apoptosis.[11] Since nanoparticles will generally exhibit different properties at less than 30nm, only those have been suggested as to require regulatory scrutiny.[12] The direct effect on health will be best determined by real-time measurement of size, shape, crystal structure, charge, surface chemistry and adsorbed species.

Agglomeration may result to produce larger particles before deposition within the respiratory tract. The size, shape and surface area may differ dramatically from the original form. Toxicity studies of tyre debris leachates reveal that the particle aggregation influences the elution process more than the quantity of particles.[13]

3. Characteristics of aerosols/ airborne nanoparticles

3.1 Aerosols from the automotive industry

The types of aerosols will differ depending on the location of the measurement. Close to major roads, the particulate will be mainly from tailpipe, resuspended road dust, brake-wear and tyre wear. Brake-wear and tyre-wear fine particulate are produced at small quantities in comparison to tailpipe emissions from on-road vehicles[17]. The major contributor will be tailpipe emissions arising from diesel operated vehicles.

A majority of the excess amount of $PM_{2.5}$ in urban areas with high population densities compared to nearby rural areas is due to carbonaceous matter. These arise from the combustion of different fossil fuels (diesel, residual oil and coal).[18] While char particles are large and carry the ingredients of the source, the finer soot particles produced from an evaporation-condensation reaction do not include other elements in the final aerosol composition, Figure 1. Therefore, the final chemistry of diesel particulate consists of more carbon. This may be used as a fingerprint to detect the source of the carbon aerosol.

The chemistry and shape of combustion aerosols may be further modified by the selection of the fossil fuel and combustion conditions. Ultrafine soot from the combustion of different fossil fuels shows the general tendency for agglomeration. Fine dense particulate develop a rounded-like morphology to minimize the surface area, and hence the overall energy of each nanoparticle. For diesel particulate these individual building blocks are about 50nm and they agglomerate to lower the total surface area.

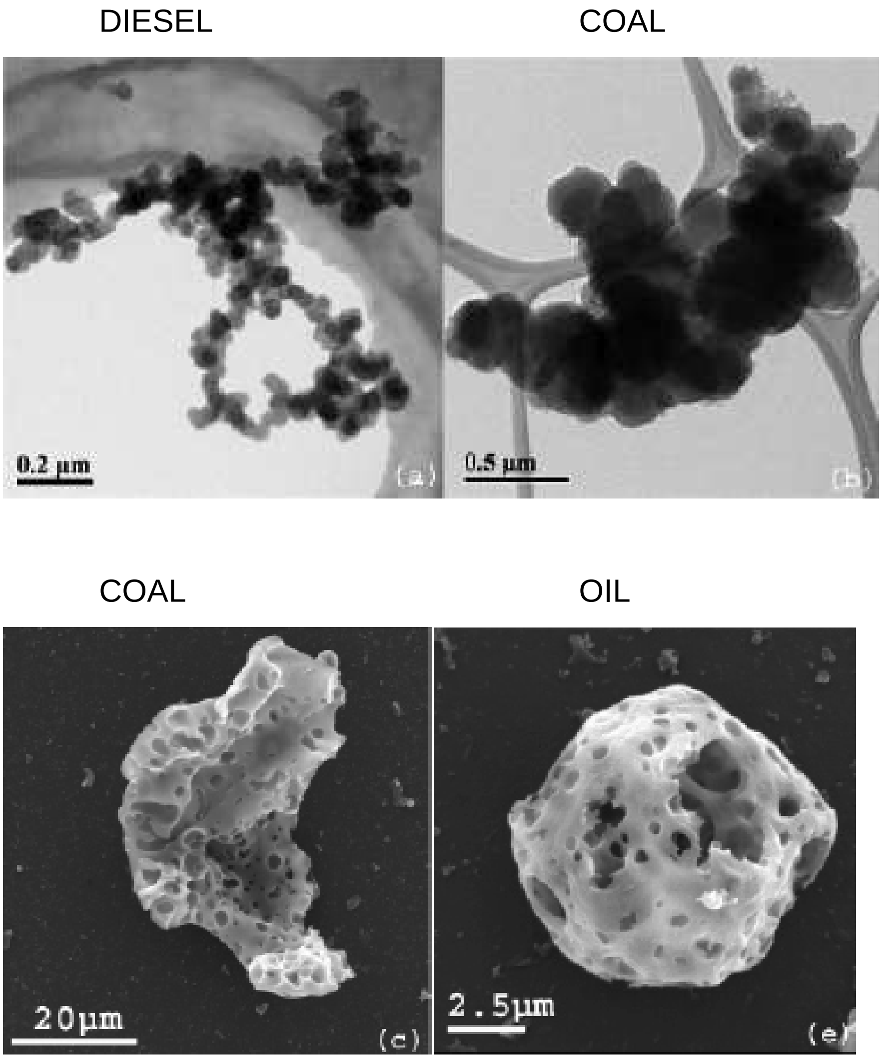


Figure 1. Aerosols from diesel emissions, combustion of coal and oil, showing the different sizes and morphologies. The larger particulate from oil and coal show a larger surface area from surface porosity.

3.2 Characteristics of particulate emissions from diesel combustion

Reference is often made to diesel emissions from the automotive industry. These have been researchers the most, hence the sourcing of information from a related field. Diesel combustions is also used in trains, aircraft, land-based electrical power generators and the focus of this document – ship emissions.

The gas emissions primarily consist of nitrogen, oxygen, water vapour, carbon dioxide, and minor constituents of CO, hydrodrocarbons, NOx, and, and particulate matter. The particulate matter, as depicted below in an artists conception by Maricq (J. Aerosol Sci., 2007, 38, 1079) shows the assemblage of the different constituents, Figure 2. The majority of the particulate consists of carbon black with covered by small amounts of sulphate. Condensed water is not shown in the figure, and will not appear until an interaction with a cooler surface or cool air. Carbon black is primarily graphitic in form, but a small amount consists of organic carbon.

The composition of the fuel will dictate variations from the model below. Fuel with a higher sulphate content will lead to greater amounts of condensed sulphate. Heavy fuel, used by ships far away from land has a large amount of sulphates, and so the deposit will be rich in a viscous sulphate phase together with solid graphitic particles that may be individually includes in the sulphate. The microstructure of the aerosols has not been reported.

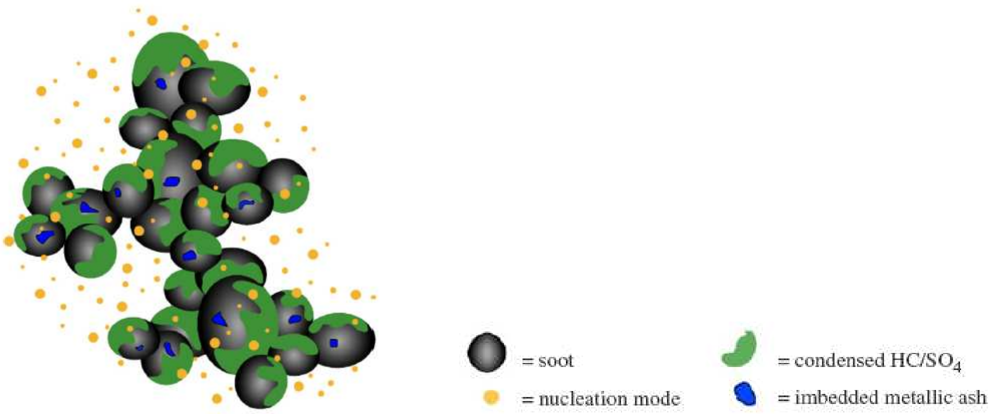


Figure 2. An artists conception of soot, drawn by Maricq (J. Aerosol Sci., 2007, 38, 1079).

Other constituents, such as heavy metals that are added to the fuel also emerge in solid forms at a low concentration, as well as metals salts (van Setten et al. Catalysis Reviews, 2001, 43, 4, 489)). More information will be provided on this later.

Commercial ships, enroute and at port, release more sulphur dioxide particulate than all of the world's cars, trucks and buses combined, according to a study released in March by the International Council on Clean Transportation, and quoted in a Wall Street Journal article Nov. 27, 2007. The study further found that ships produced an estimated 27% of the world's nitrogen oxide emissions – a huge percentage by any standard.

In November, 2007, a peer-reviewed study in the American Chemical Society's journal, Environmental Science and Technology estimated that under-regulated air pollution from ships results in 60,000 deaths from lung cancer and cardiopulmonary disease each year, primarily along trade routes in Asia and Europe.

4. Real-time Measurement of Aerosols

The reference methods, based on the manual weighing of filters, are clearly unsuited to real-time automated data production that can be disseminated to the public in the same way as for gaseous pollutants. Commonly used automatic methods across Europe include Tapered Element Oscillating Microbalances (TEOM), which measure the increasing mass of a filter by its effect on the resonant frequency of a vibrating support; beta attenuation monitors, which measure the increasing amount of material on a filter by its absorption of electrons emitted by a weak beta-source; and optical monitors, which can gauge the size of individual particles from signals scattered from a light beam and integrate this into a total volume of particles.[27] These methods do not have the sensitivity to measure small concentrations, or small nanoparticle sizes in real-time that are crucial for today's requirements.

The opacimeter is a simple sensor useful for engine development, inspection and maintenance of related particle measurements, where often only relative quantities of the emission are required. The opacimeter (e.g. ISO 3173, SAEJ1667), commonly used in inspection tests, measures extinction of light in the exhaust gas in the visible or near infrared wavelength regions. A more modern technique capable of on-line soot measurements is laser induced incandescence (LII).[28] The measured soot containing flow is illuminated with a pulsed laser source and the blackbody radiation from the heated soot particles is detected. LII can be used as an imaging measurement, enabling both spatial and temporal measurement of the soot volume fraction and primary particle size of the soot, as demonstrated by Will et al.[29] The measurement can be used to study the soot formation inside the flame region of a combustion process. Other promising and relatively simple instruments are the photoacoustic sensor[30] and the diffusion charger.[31] The photoacoustic sensor utilizes the high absorption coefficient of the soot and measures acoustic signals originating from the particles heated by pulsed light source. With the diffusion charger measurement. the particles are charged in an unipolar corona discharge charger and then collected with a Faraday cup filter. The charge on the particles is measured as a current signal. The outcome of the diffusion charger measurement is related to the total active surface of the aerosol measured.

In general, electrical measurement methods seem promising, when aiming towards a simple sensor solution for aerosol measurement. The simplicity and ruggedness of the electrical measurement methods are the key properties. Electrical measurement methods also provide fast response times, which make it possible to use them in real time measurements of a changing aerosol. With electrical methods, the particle size or the concentration cannot be measured directly. If the measured aerosol and the properties of the sensor are known, the measured electrical signals can be converted for instance into a number or mass concentration. In emission measurement, the temporal concentration values need to be converted into temporal emission rate values (#/s, mg/s), integrated over time and divided by the produced energy or travelled distance. The current regulations for particle emissions are based on total mass (mg/km, mg/kWh). A proposal for particle number emission measurements (#/km, #/kWh) is included in future Euro V/Euro VI regulations (Regulation (EC) No 692/2008).

5. Charging of Aerosols

Corona discharge is among the most common technique to produce high ion concentrations. There have been numerous studies in the past and used in many industrial applications such as electrostatic coating and precipitation. Electrostatic charging by the corona dischargers is also common in aerosol size determination by electrical mobility analysis. Corona discharge is produced by a nonuniform electrostatic field such as that between a needle and a plate or a concentric wire and a tube. Air and other gases can undergo electrical breakdown when the electric field strength is high. For the case of the wire and the tube, the only place this breakdown can occur is in a very thin layer at the wire surface. In this corona region, electrons have sufficient energy to knock an electron from gas molecules creating positive ions and free electrons. During this process, aerosol particles flow is directed across the corona discharge field and is then charged by attachment of ions produced by the corona discharge. Ions are transported by the electric field and/or by thermal diffusion. Particle charging due to the ions transported by electric field is called ‘‘field charging’’. For supermicron particles (>1 mm), field charging is dominant. For ultrafine particles (<0.1 mm), thermal diffusion becomes dominant, and ‘‘diffusion charging’’ becomes important. For the size range in between, both mechanisms show varying degree of effect. The amount of ion deposition on the particle surface depends on resident time, particle radius and shape, electric field, etc. This technique has been applied successfully and several designs of aerosol corona charger are employed and described in the published literature, both corona-wire and corona-needle chargers. There is a growing need to characterize particles at smaller sizes. Diffusive losses of nanoparticles become an issue as one approach the nanoparticle size and should be noted for particles less than 20nm. The uncertainty of charging inside a unipolar electrical aerosol chargers is 14% for 2.5nm sized aerosols, and decreases to 4% for 10nm sized aerosols.[32]

A number of particle sizing instruments employ unipolar corona chargers as important upstream component to impart known charge to the aerosol system. Generally, the ideal charger would need to have (i) high ion concentration, (ii) no gas-to-particle conversion and low coagulation between charged particles,

(iii) low particle losses, (iv) no contamination, (v) applicability to nanoparticles, and (vi) ability to work at various conditions.

A typical corona discharger is shown in Figure 3 and typical charger characteristics are given in Table 1.

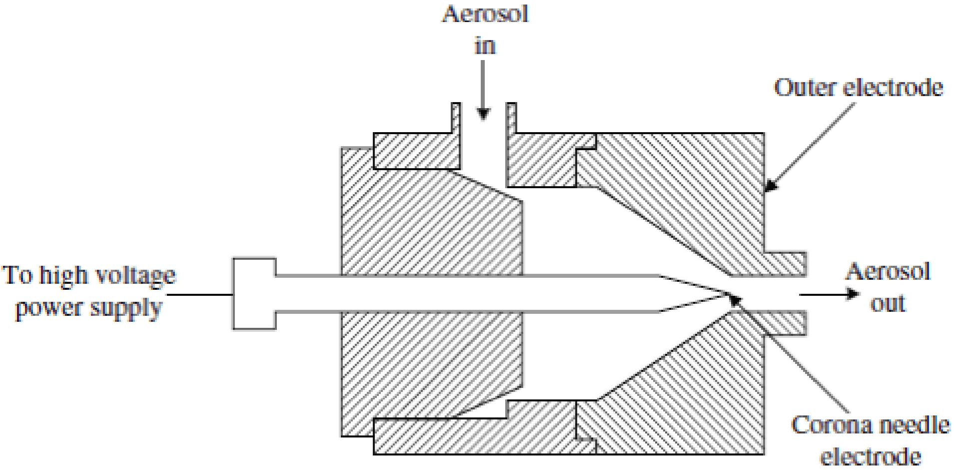


Figure 3. Typical corona discharger

Table 1. Typical charger characteristics for different charger designs.

Reference	Corona electrode	Inner electrode diameter	Outer electrode diameter	Aerosol flow rate	Sheath air flow rate	Electrode voltage range	Polarity	Nt product	Aerosol/ion direction	Charging efficiency
Hewitt [4]	Wire	n/a	n/a	n/a	No	n/a	n/a	n/a	Perpendicular	n/a
Liu et al. [6]	Wire	n/a	n/a	n/a	No	n/a	Positive	n/a	Perpendicular	n/a
Liu and Pui [7]	Wire	25 μm	n/a	4 L/min	1 L/min	n/a	Positive	1×10^{6}–3×10^{7} s/cm^3	Perpendicular	1.1% at 6 nm
Buscher et al. [10]	Wire	n/a	30 mm	2 L/min	0.5 L/min	4.5 kV	Positive	1.1×10^{7} s/cm^3	Perpendicular	4% at 5 nm
Unger et al. [11]	Wire	330 μm	14 mm	2–6 L/min	No	8.5 kV	Negative	n/a	Perpendicular	n/a
Kruis and Fissan [12]	Wire	25 μm	16 mm	n/a	No	n/a	Positive	1–8 $\times 10^{7}$ s/cm^3	Perpendicular	30% at 10 nm
Biskos et al. [13–15]	Wire	76 μm	74 mm	5 L/min	n/a	2–9 kV	Positive	3×10^{7} s/cm^3	Perpendicular	60% at 20 nm
Intra and Tippayawong [16]	Wire	300 μm	28 mm	1–5 L/min	No	5–10 kV	Positive	1.5–4 $\times 10^{7}$ s/cm^3	Perpendicular	n/a
Whitby [17]	Needle	n/a	n/a	70 L/min	No	0–9 kV	Positive/negative	n/a	Perpendicular	n/a
Medved et al. [18]	Needle	n/a	n/a	n/a	n/a	n/a	Positive	n/a	Perpendicular	40% at 10 nm
Marquard et al. [19]	Needle	n/a	n/a	n/a	n/a	n/a	Positive	n/a	Perpendicular	n/a
Hernandez-Sierra et al. [20]	Needle	3 mm	4 mm	0–10 L/min	No	2.5–4 kV	Positive/negative	n/a	Perpendicular	30% at 10 nm
Alonso et al. [21]	Needle	n/a	3.5 mm	0–10 L/min	No	3.1–3.7 kV	Positive	1–4 $\times 10^{7}$ s/cm^3	Circular	55% at 13.6 nm
Intra and Tippayawong [22,23]	Needle	3 mm	4 mm	0–5 L/min	No	3–5 kV	Positive	2–8 $\times 10^{7}$ s/cm^3	Circular	n/a
Park et al. [24]	Needle	0.25 mm	n/a	5 L/min	5 L/min	3.5–5 kV	Positive	1–7 $\times 10^{7}$ s/cm^3	Perpendicular	n/a

n/a: information not available.

6. Real-time Sensing of Particle Surface Area

The risk of nanoparticles by inhalation for human health is still being debated but some evidences of risk on specific properties of particles below 100 nm in diameter exist. One of the nanoparticle parameters discussed by toxicologists is their surface area concentration as a relevant property for e.g. causing inflammation. Concentrations of these small particles (< 100 nm) are currently not measured, since the mass concentrations of these small particles are normally low despite large surface area concentrations. Airborne particles will always be polydisperse and show a size distribution. Size is normally described by an equivalent diameter to include deviations in properties from ideal spherical particles. Total concentration measures are determined by integration over the size range of interest. The ideal instrument should measure the particles according to the size weighting of the wanted quantity. Particle surface area, or more accurately total aerosol length can be measured in real time by giving particles saturation surface charge by diffusion of ions. Unfortunately aerosol length is not generally accepted as scientific a measure. For this reason instrument manufacturers have started to report active surface area of particles, which is hoped to gain acceptance among different communities.

Most likely total mass and total number of particles will be the quantities to be requested by authorities also in the future. This applies especially to authorities among engine emissions, stack emissions and ambient air PM communities. The only area of industry where regulated quantity is not yet defined and surface area has some potential is industrial hygiene and especially nanoparticle production. The reason for this is the good correlation between lung deposition and total surface area of particles. Globally there are several joint consortiums addressing this matter. Unfortunately there are no definite deadlines for proposals. For this reason these committees will most likely run for several more years before any definite decisions are made. There is fair chance that surface area of particles will be used as supporting quantity in addition to total number of particles.

7. A Growing Need for Surface Area Monitors

The smallest particles, less than 100 nanometers, may be very damaging to the cardiovascular system. There is evidence that particles smaller than 100 nanometers can pass through cell membranes and migrate into other organs, including the brain. It has been suggested that particulate matter can cause similar brain damage as that found in Alzheimer patients. Particles emitted from modern diesel engines (commonly referred to as Diesel Particulate Matter, or DPM) are typically in the size range of 100 nanometers (0.1 micrometer). In addition, these soot particles also carry carcinogenic components like benzopyrenes adsorbed on their surface. It is becoming increasingly clear that the legislative limits for engines, which are in terms of emitted mass, are not a proper measure of the health hazard. One particle of 10 µm diameter has approximately the same mass as 1 million particles of 100 nm diameter, but it is clearly much less hazardous, as it probably never enters the human body - and if it does, it is quickly removed. Proposals for new regulations exist in some countries, with suggestions to limit the particle surface area or the particle number.

7.1 Occupational Safety

Industrial hygiene has not been able to make up its mind on reported quantity. Traditionally total mass and total number of particles is set as limit values. In order for these to change to, or to be complemented by particle surface area, verification work is needed. In the next three years, measurement of surface area by the research community will explore the relationships with number and mass concentrations.

Measurement of exposure will be required to protect the health of workers that are increasingly becoming aware of airborne particulate from existing sources or new nanotechnology operations. It is estimated that 10 million people will have nanotechnology-related jobs by 2014.[34] Present measurement capabilities do not provide the required performance based on the detection limit or because they are bulky and are not available for in-situ and field-based environmental monitoring. Furthermore, they are usually large instruments that require operator training for correct interpretation of the data. Some hand-held devices are available, such as a condensation particle counter,[35] however these can be placed on a bench and no longer assess the nanoparticle condition for the worker. Lapel-like sensors, not available at this point in time, will provide better monitoring, but require developments for miniaturization of the device.

Many reports have shown that the surface area determines the toxicity. A direct correlation has been established between inflammation in the lung and surface area, measured by BET.[36] As a result, wearable sampling devices would not only measure the conventionally reported aerosol measures, the number and mass concentration, but also offer a report of the surface area.[33] For a nanomanufacturing installation, where the characteristics of the nanoparticles have been well determined, a change in the nanoparticle size will be best measured by the number concentration, but more detailed information obtained from the surface area, that can detect the change in particle shape and surface area. Measurements on control aerosols will reveal the change in the surface area distribution that arise from changes in the particle size, shape and surface porosity.

Progress in the fields of sensing, communications and electronics will see the inclusion of different sensing capabilities. Some of these are already being integrated into the mobile phone that is providing a contact point for examining the information, and may have the option of furthering notifying other bodies if the reported value is at a critical level. Such a device will need to be small, well integrated in the communication network and have the potential of activating warning systems where dangerous work conditions are suddenly identified. The combination of sensors on work equipment with sensors on people will provide the capability to quickly identify the source of the dangerous nanoparticle emissions as well as the location of people.

The introduction of such sensors will initially involve the sensor together with the reporting device. Mobile-phone-like devices can be distributed within a work environment to independently collect and examine the nanoparticle traffic. This arrangement provides the required power source for operation of the sensor. If a trend from other sensing technologies can be applied to aerosol detection, then extra low-cost sensors will be available requiring very low levels of power and air movement for their operation. These will be integrated into a communication network to provide the status of airborne nanoparticles at numerous locations. Communication systems have been developed that will continue to operate when individual sensors cease functioning. The combination of aerosol sensing, communication protocols, microfabrication and microelectronics will lead to improved nanoparticle monitoring for improved working conditions of employees in nanotechnology installations. This capability has been absent in the working conditions of scientists and engineers who have been involved with new nanoparticles, leaving an unknown effect on the health status.

The introduction of new alternative solutions in medical clinics will undergo closer scrutiny with the introduction of better means of assessing the nanoparticle population. Medical consumables will undergo more scrutiny. Sterile latex gloves, both powdered and powder free, previously assessed by gravimetric methods[37], need to be assessed by more sensitive techniques. The interest in these measurements already exists, and a simple sensor can lead to more measurements in the future, that could become standard practise.

7.2 Vehicle emissions

Despite the interest among researchers, total sales potential of instruments reporting total surface area will remain low for the next three years. This is true for engine emission markets where clear statement has been made by several respected sources that they will not promote surface area measurement for the industry (Renault, Ford, PSA Citroën). Also for ambient air and stack emission monitoring there is no sign of projects looking at surface area measurement to start or requested by financing institutions.

It is advised that total surface area monitor manufacturers should try to correlate the surface area signal to legislative quantities such as total mass or total number of particles. This is impossible without measuring information on the particle size distribution (Geometric Mean Diameter GMD, Geometric Standard Deviation GSD).

7.3 Shipping

In 2003, land based emissions continued to be reduced, but emissions at sea continued to increase. The European Maritime Safety Agency has noted a lack of integration between the European Union transport and environmental policies.[38] HELCOM Maritime WG, at the second meeting in Stockholm in January 2004, accepted the recommendation on pollution prevention, shipping safety and shipping influence on the environment.[39] A Satellite based monitoring system has been introduced for the surveillance of pollution in European waters (CleanSeaNet). The integration of satellite traffic maps (Figure 4) and pollution will provide the first step in coming closer to a system for regulation of the airborne pollution. The second involves the introduction of filtration systems, and sensing equipment. Many sea freight carriers have old technology and will be able to integrate cheap, effective monitoring sensors.

Ship emissions contribute substantially to atmospheric pollution over the summertime Mediterranean region, mainly in the Western Mediterranean, Figure 6. Since sulphate aerosols are short-lived, they will only have an effect within Europe.[40] Studies at the Max Plank Institute for Metereology show that the contribution of the sulphate aerosol over the Mediterannean sea is 7.8 mg/m^2, compared to an average of 4.7 mg/m^2 in Europe. Sulfate aerosol particles scatter incoming short wave radiation, effectively raising local planetary albedo, thereby cooling the earth-atmosphere system (Haywood and Boucher, 2000). Despite this benefit to cooling, the sulphate contributes to acid rain and so needs to be reduced to protect monuments and architectural features of historical significance. Sulfur oxides in ship fuel can be reduced cost effectively, and future monitoring is needed. A reduction in

SO_2 PM will reduce the number of deaths by 50% from 80,000 in a prediction made for 2012.[41]

A total of 0.05% of the fuel is emitted as particulate matter, with a bimodal particle size centred at 500nm and 7 µm. Particulate matter contains organic carbon, ash and sulphate, and elemental carbon that is present at a few percent of the total particulate matter. Exhaust cooling produces more organic carbon & sulphates.[42] The indirect aerosol effect of ships on climate is found to be far larger than previously estimated contributing up to 39% to the total indirect effect of anthropogenic aerosols.[43]

Each ship produces a high concentration of aerosol pollution, and so requires an aerosol sensor. The number of ships will place a ceiling on the number of sensors required within the industry. A larger impact can be made by land-based individuals who produce airborne particulate from diesel car/truck emissions or heating with firewood.

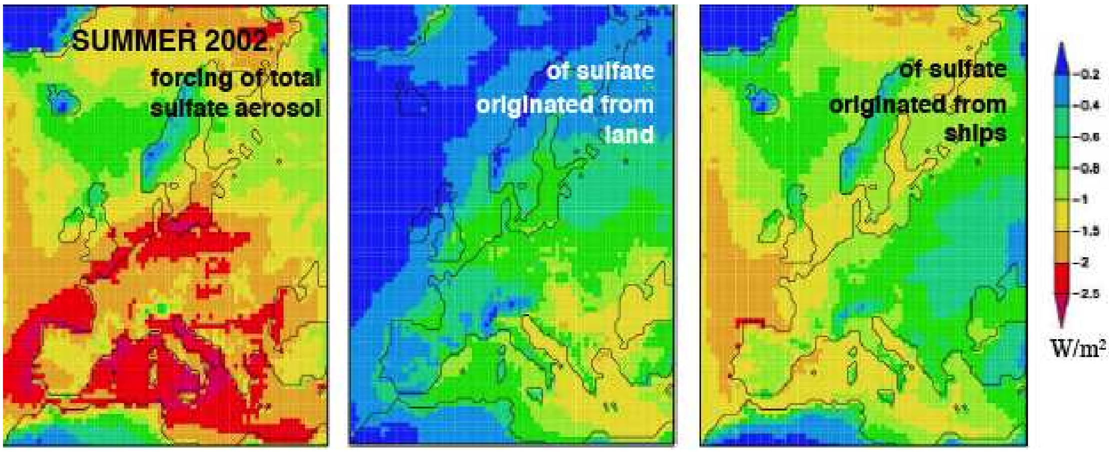


Figure 4. Impact of ship emissions on direct radiative short wave forcing. More than 50% of direct radiative forcing over the Mediterannean sea is attributed to sulphate based aerosols from ships. Figure obtained from a study at the Max Plank Institute for Meteorology.

The EPA finalized a ruling on tough engine and fuel standards, a major achievement significantly to lower marine diesel emissions.[44] A predicted increase in port traffic will demand new measures such as smoother and faster exchange of cargo vessels and tighter requirements on environmental pollution. By 2030, the international strategy is to reduce the present air particulate emissions by 143,000 tons. This will effectively lead to an 85% reduction in particulate emissions from ships.

7.4 Aircraft emissions

While diesel engines are favoured for the efficiency, torque and overall driveability they suffer from more noise, nitrogen oxide and particulate emissions. The greater se of diesel engines in conjunction with the other undesirable effects is refocusing attention at the soot formation process to reduce the undesirable emissions. Aircraft engine particulate exhaust emissions tend are characterized by a trimodal size distribution. The largest mode was dominated by ambient accumulation mode particles. The middle mode contained carbon soot with sulphate and organic carbon films, but the smallest mode was completely volatile and consisted of sulphate and organic components.[46] Soot formation is more influenced by the oxygen level within the fuel, the entrained air in the jet and combustion temperature as opposed to the composition and structure of the hydrocarbons in the fuel. Lower temperature and better air/fuel mixing prior to ignition will avoid the nitrogen oxides and soot formation.[47]

8. Known Surface Area Measuring Instrument Manufacturers

Table 3 lists known instruments that measure total surface area of particles. Well known ELPI and SMPS and its several commercial variations are left out from the table since they are mostly used to measure particle size distribution weighted on mass or number.

The meDISC (Matter Engineering) charges particles that pass through three measurement stages. In Stage 1 (diffusion stage), small particles deposited on grid and therefore limits the time of operation before cleaning. Stage 2 (induction stage) has no deposition of aerosols, but Stage 3 (filter stage) has particle collection on a filter. Currents from the charged particles are measured with amplifiers at three stages.

TSI has made a leap by providing an instrument with a readily understood measure by the medical profession. A modification of the EAD is the Nanoparticle surface area monitor (Model 3550), that transforms the results in two values: the tracheobronchial fraction and the alveolar fraction. This provides measures of particles deposited in the different parts of the respiratory system. The particle size range measured is 10-1000 nm at a rate of 1 measurement/second

A comparison of the performance characteristics shows that the Pegasor Particle Sensor (PPS) measures to a lower particle size, can measure a greater concentration range and can do so faster that other instruments. Consumables are not necessary, allowing the PPS to be placed into difficult to access locations. The sensor geometry will become an important part of the PPS, to prevent aerosol deposition over a range of operating conditions. Investigations at higher temperatures will establish a sensor that can be used more in a wider range of testing conditions.

Table 2. Electrical sensing aerosol instruments and their characteristics.

	PPS	**meDISC***	**EAD****	**NanoCheck**	**ETaPS**
Supplier	Pegasor	Matter Eng	TSI	Grimm	Dekati
Temp range (^oC)	0 - 850	3 – 35	10 – 40	10 – 40	< 400
Conc range	1 μg/m^3- 250 mg/m^3	$10^3 – 10^6$ part/cm^3	$10^2 – 10^8$ part/cm^3	$10^3 – 10^6$ part/cm^3	100 μg/m^3 – 100 mg/m^3
Part size (nm)	few nm – 2500	20-200	10-1000	25-300 25 - 20000	N/A
Time resol (sec)	0.01	2	0.25	10	0.5
Operating power (W)	0.5	40	N/A	battery	5 W
Sensor output	mg/m^3, part/cm^3	1/cm^3 and size of	mm/cm^3	# conc, mean size,	0-10 V

		particles		active SA	
Consumables	-	Filter every 8 days	Carbon & HEPA filter	Battery	-

9. Legislation on aerosols

Legislation has led to the certain limits of particulate matter to be emitted by manufacturing industries, the transportation sector and the heating industry. The first established measure was PM10, representing particulate matter less than 10 microns. With time, it was seen that smaller particle sizes had an effect on health, and this has led to legislation on the use of PM2.5, particulate matter less than 2.5 microns. PM2.5 is now more widely used, and presents the latest aerosol measure. Together with the concentration of aerosols, particle size/mass have been sole measures of acceptable levels of nanoparticulate/aerosol indoor or outdoor air quality.

Different techniques are available for the measurement of aerosol size and concentrations. The scanning mobility particle sizer (SMPS) and the electrical low-pressure impactor (ELPI) have been used to measure particle size distributions of diesel soot. Results show that the SMPS underestimates the diesel agglomerate size, while the ELPI overestimates the number of aerosol particulates.[48] This requires a modification in the way in which the measurement is taken, or a new aerosol measure.

Another measurement technique may be used to report on the aerosol characteristics. For health considerations, the bioavailability of the aerosol components is dictated by both the surface area and the solubility. The surface area has been used as a basis for several new instruments in the marketplace. Such an instrument may offer the detection of pores in the outer surface, or the formation or high surface area crystals on the nanoparticle surface.

The fast response time and high temperature capability of the PPS provide a sensor with the capability to follow the ignition cycle in the combustion engine for closer analysis of the combustion under different conditions. Furthermore, the small size and low power requirements make it ideal for an on-board sensor operation. Legislation in USA defined the monitoring requirements in 1998 in a document entitled "Modification of Federal Onboard Diagnostic Regulations for Light Duty Vehicles and Light Duty Trucks". New thresholds were applied in California is 2004. For Japan, legislation was introduced in October 2000 for new cars, and then applied to all other cars running on both gasoline and diesel. In Europe, legislation required on-board sensors in all cars from January 2004.

Proposals for new regulations exist in some countries, with suggestions to limit the particle surface area or the particle number. The following shows the transition to particle number, a trend that may well repeat itself with more information from surface area measurements in the future.

There has been considerable progress in developing a standard for measuring particle numbers – the so-called Particle Measurement Protocol or PMP, and the time is ripe to develop standards for PM numbers. It is important that the standard enters into force way before Euro 6, in order to give a clear signal that Euro 5 vehicles will also be subject to particle number testing and only good filters should hence be fit. *“The PMP particle number measurement system has been demonstrated to be repeatable and reproducible between laboratories. The validation programme results clearly indicate the particle number performance level attainable by diesel particulate filter (DPF) equipped vehicles of all sizes and the vehicle-vehicle variability. The measurement system has proven itself to be stable and robust.”* Therefore PM number standards could and should enter into force by 2010. *“The particle number measurement technique is therefore suitable and useful for regulatory purposes.”*

Legislation firstly required the total suspended matter to be measured, and this was followed by PM10, and then PM2.5. Now, there is a trend from mass measurements to number measurements. This will be possibly accompanied by surface area measurements. The added benefits of small size, operation at high temperature, lower power requirements, integration of the small sensor into another operation, use as an on-board sensor and a wide particle size measurement range positions the Pegasor Particle Sensor as a very competitive sensor for applications requiring aerosol measurement.

New regulations are being put into place to limit the emissions from sea going vessels. The emissions include NO_x, SO_x and airborne particulate. The primary targets are SO_x and NO_x, but a proposal to the IMO indicates that these are linked to fine particulate matter. Regulation 14 on the Requirements for Control of Emissions from Ships, from a Revised MARPOL Annnex VI document points to the reduction of suphur oxides and particulate, but only specifies the requirements on sulphur oxides. The sulphur contect of any fuel oil used on board ships shall not exceed

4.5% m/m up to Jan 2012
3.5% m/m after Jan 2012
0.5% m/m after Jan 2020

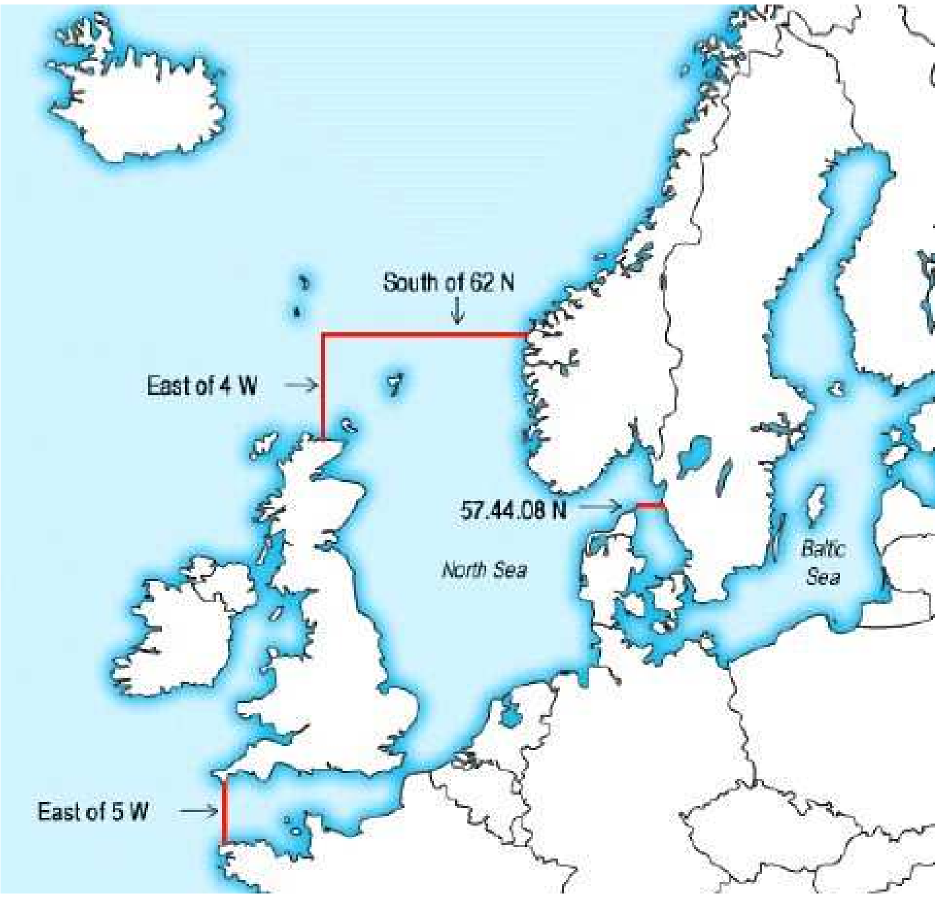
These requirements are more stringent in ports and emission control areas, as document in a Sustainable Shipping Briefing paper from August 2009. The three major emission control areas (ECA) include the Baltic Sea, the North Sea and the cost of USA and Canada. These areas are shown in Figure 4. Ships must use a fuel with a sulphur level less than 1.5% or fit an exhaust scrubber. In an ECA, the maximum sulphur level in a fuel must be

1% m/m on or after Jul 2010 and
0.1% m/m after Jan 2015

Stricter requirements are in place for the coastline of California. Ocean-going vessels operating within 24 nautical miles of California are only allowed a maximum of 0.5% suphur in fuel to be used in their main engines, auxiliary engines and auxiliary boilers. The California Air Resources Board are reducing this level to 0.1% beginning January 2012.

Present requirements for ships in ports are at 0.1%, indicate that seagoing vessels can switch from different fuel types. Increasing restrictions will lead to a more sustainable industry, where the suphur is extracted within the fuel refinery, where it can be reused, providing a cleaner environment.

USA and Canada want an 85% reduction in OM by 2015. At the current emission performance, 115,000 tonnes of PM are produced by ships within 200 nautical miles. The cost for switching vessels from residual fuel to 0.1% sulphur fuel will cost $145/tonne, but $6/tonne for an change from 0.5% sulphur fel to 0.1% sulphur fuel.



(a)

(b)

Figure 4. Emission control areas for (a) The Baltic and North Sea areas and (b) the shoreline of Canada and USA.

10. Concluding Remarks

Globally, ships emit large quantities of particle pollution into the air every year. "Since more that 70% of shipping traffic takes place within 250 miles of the coastline, this is a significant health concern for coastal communities".

Legislation in the shipping industry is pointing to a reduction in the sulphur content of fuel to be used on seas going vessels. Real-time particulate monitoring will play an important role for the shipping industry. These are not presently available, but a review of the present capabilities shows the emergence of new technology in the marketplace. The commitment of the automotive industry to develop onboard diagnostics sensors will lead to better monitoring of airborne particulate on seagoing vessels and assist the introduction and operation of air particulate filters.

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