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Exposure to nanomaterials from the Danish Environment

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Exposure to nanomaterials from the Danish Environment

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Preface

Nanomaterials (NM) are found in a wide range of consumer products and the commercial use of nanomaterials is anticipated to increase rapidly in the near future both in quantity and diversity. It is increasingly recognised that materials in the nanoform can have unique properties as compared to the microforms and macroforms of the same material. This favours the use of NM in products, articles and technologies. At the same time, concerns in relation to the possible health and environmental properties and impacts of NMs have surfaced.

On this background, the Danish government and the Red-Green Alliance (a.k.a. Enhedslisten) have signed an agreement for four years (2012-2015) that focuses on the use of NM in products available on the Danish market and their impact on consumers and the environment.
The Danish Environmental Protection Agency (EPA) has initiated a series of projects with the aim of further clarifying possible risks to consumers and the environment.

The current project addresses consumer exposure and risk assessment of nanomaterials in products on the Danish market. It runs from third quarter 2013 through second quarter 2015.

The project is foreseen to result in four reports:

- Exposure assessment of nanomaterials in consumer products
- Hazard assessment of nanomaterials in consumer products
- Human exposure to nanomaterials in the environment – as a reference to nanomaterials exposure from consumer products (the current report)
- Consumer risk assessment and overall conclusions (final report).

The first three reports will be finalised during 2014, whereas the final report with the consumer risk assessment and overall conclusions will be finalised in the second quarter of 2015.

The overall project has been implemented with support from a reference group:

- Susan Dekker, National Institute for Public Health and the Environment (RIVM), The Netherlands
- Andrea Haase, Bundesinstitut für Risikobewertung (BfR), Germany
- Gregory Moore, Swedish Chemicals Agency (KEMI), Sweden
- Derk Brouwer, Netherlands Organisation for Applied Scientific Research (TNO), The Netherlands
- Lena Høglund (Danish EPA)
- Katrine Bom (Danish EPA)
- Anne Mette Boisen (Danish EPA)
- Kim Petersen (Danish EPA)

The reference group has assisted with comments and ideas, but is not responsible for the content of the project reports.

This report covers human exposure to nanomaterials in the environment – as a reference to nanomaterials exposure from consumer products.

The report has been made in close collaboration between DHI and COWI and been elaborated by:

- Poul Bo Larsen, DHI (project leader)

- Jesper Kjølholt, COWI

While quality assurance has been conducted by:

- Henrik Rye Lam, DHI
- Carsten Lassen, COWI

During the elaboration of the report comments have been received from:

- Kim Pedersen, Danish EPA (Danish EPA responsible for the overall project)
- Anne Mette Boisen, Danish EPA
- Christian Lange Fogh, Danish EPA

Summary and conclusions

Under the Agreement "Better Control of Nanomaterials" (“Bedre styr på nanomaterialer”), the Danish EPA has commissioned a number of projects aiming to investigate and generate new knowledge on the presence of nanomaterials in products on the Danish market and assess the possible associated risks to consumers and the environment.

This report is part of a series of four from a project, which addresses consumer exposure and risk assessment of nanomaterials in products on the Danish market.

The aim of this work package of the project is to evaluate the population’s exposure to nanoparticles from the environment i.e. ambient air, indoor air, soil and water (drinking water) and to describe the risk associated with this exposure. The results should give proportionality to the possible risks from exposure to nanomaterials from use of consumer nano-products which are described in other parts/ work packages of this project.

This report will summarise current knowledge on risk to Danish consumers from the environment and cover:

- Survey reports and summarize the exposure and risk to consumers from incidental nanoparticles from traffic combustion and other sources e.g. indoor air of particulate air pollution
- Survey literature on current nanoparticle presence in drinking water and soil and asses the exposure of consumers from these sources

Ultrafine particles in ambient air

There is a general consensus that ultrafine particles are defined as particles smaller than 100 nm in mobility diameter. In this report, they are considered non-engineered nano-sized particles present in ambient air. Increased levels of these particles in urban settings mostly stem from combustion processes i.e. traffic exhaust and wood burning.

From epidemiological studies it has been shown that measurement of the PM2.5 (the mass of particles (in mg/m^3) with a diameter below 2.5 μm) levels in general is the metric that is best correlated to adverse health effects of ambient air particulates. The association between PM2.5 (also termed fine particles) and health hazards has put focus on the smaller size fractions of particulate matter, including the ultrafine particles. The ultrafine particles can either be measured on a mass basis (referred to as PM0.1 in mg/m^3) or they may be measured on a number basis (particle number/cm^3). Due to the very small mass of ultrafine particles the weight of these (expressed as PM0.1) they only contribute with a small fraction in PM2.5 or PM10 (particle up to 10 μm in diameter) measurements.

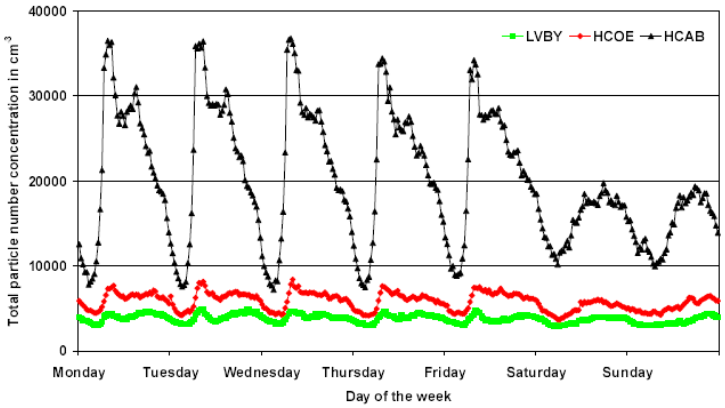
As ultrafine particles are very unstable in air (due to rapid agglomeration into larger particles), high spatial variation pertains to the measurements of ultrafine particles. Thus, the concentrations of ultrafine particles rapidly decline with increasing distances from the emission sources (roadways, wood stoves etc.). The levels of ultrafine particles often differ substantially from one location to another within the same city. Due to their small contribution to mass (e.g. measured as PM2.5), ultrafine particles are not well reflected in PM mass measurements and they are not routinely monitored in most locations. Thus, exposure estimates for the population to ultrafine particles based on data from fixed located measuring stations, are subject to substantially more uncertainty

and error than measurements for PM2.5 and PM10, where the levels are subject to less spatial variation within a geographical area.

Despite the high spatial variability of ultrafine particles, the number concentrations measured at various locations within cities tend to be reasonably correlated in time, rising and falling in similar patterns over the course of a day.

Levels of ultrafine particles in ambient air

The high diurnal variations in levels of ultrafine particles (measured as particle number/cm^3) in urban air can be illustrated by the figure below showing the fluctuations of the ultrafine particles at a busy road in Copenhagen (HCAB up to 36 000-37 000 particles/cm^3), at urban background level in Copenhagen (HCOE up to about 8000 particles/cm^3) and at rural background level (LVBY up to about 5 000 particles/cm^3) (NERI 2011).



DIURNAL VARIATION OF TOTAL PARTICLE NUMBER CONCENTRATIONS OF ULTRAFINE PARTICLES. BLACK CURVE: BUSY STREET. RED CURVE: URBAN BACKGROUND. GREEN CURVE: RURAL BACKGROUND. (NERI 2011).

In 2011, the annual average rural background levels were around 4 000 ultrafine particles per cm^3. The air at a busy street in Copenhagen contains additional 11 000-14 000 particles per cm^3 compared to the rural background, whereas urban background contains additional approximately 2000 particles per cm^3 compared to rural background annual levels.

In 2011 the average level of PM2.5 in Copenhagen (at the busy road) was about 20 µg/m^3 and the average number concentration was about 15 000 particles /cm^3, whereas, in rural background the figures were about 15 µg/m^3 and 4 000 particles/cm^3.

Sources and Composition

NERI (2011) indicates the following sources considered especially responsible for levels of ultrafine particles in ambient air:

-Biofuel combustion (domestic wood burning, forest fires etc.)
-Oil combustion
-Coal combustion
-Vehicles
-Secondary organic particles generated from oxidation of VOCs and semi-VOCs

For other sources e.g. *inorganic salts* and *mineral particulates,* it is very uncertain how much they contribute to the levels of ultrafine particles in the air.

No specific estimations have been made regarding the various emission sources and their relative contribution to the emission of ultrafine particles in Denmark. For the annual Danish emissions of

PM2.5 in 2005, however, the contribution from the following sources has been assessed to (DMU 2009):

-Traffic exhaust	13% of PM2.5 emissions (about 3 500 tonnes PM2.5)
-Domestic wood burning	64% of PM2.5 emissions (about 1 7 000 tones PM2.5)
-Other combustion	14% of PM2.5 emissions (about 3 700 tonnes PM2.5)

It may be anticipated that very large mass based fractions of these combustion related sources are emitted as ultrafine particles, which then after short time in air agglomerates/aggregates into larger particles.

The ultrafine particles from combustion are mainly composed of elemental carbon, soot and organic carbon. Organic carbon particles may be generated as *secondary organic aerosols,* which are particles generated from gases of volatile organic carbons (biogenic or anthropogenic) which have reacted with atmospheric oxidants such as O_3, NO_3 or OH to form low-volatility products (particles) (NERI 2011). The levels of these combustion fractions may either be reflected in measurements of particle number (measurement of free ultrafine particles) or in mass based metrics such as black smoke, soot, elemental carbon or organic carbon, which is dominated by ultrafine particles (either as free or agglomerates particles).

In general, the combustion fractions contribute with 25-33% of the PM2.5 content in ambient air for background levels and for urban street stations.

Exposure to ultrafine particles

As indicated in the figure above, average annual exposure levels for ultrafine particles in Denmark are in the range of 4 000-15 000 particles/cm^3 for rural background and busy urban areas. Peak short-term levels of up to 180 000 ultrafine particles/cm^3 have been reported at specific hot spot locations with heavy traffic.

Thus average daily exposure from 24 hours exposure to outdoor ultrafine particles would for an ***adult person*** with a daily ventilation volume of 20m^3 result in daily exposure of 8-30 x 10^{10} particles per day or for a person weighing 70 kg exposure would be ***1-4 x 10^9 particles/kg bodyweight/day***.

For ***small children*** the exposure is higher as their inhalation rate is higher compared to adult. Thus, children (1-5 years old) inhaling 0.5 m^3/kg bodyweight/day would be exposed to ***2 – 7.5 x 10^9 particles/kg bodyweight/day.***

It has however to be noted that such exposure figures only give indication of the exposure level of exposure to free ultrafine particles, and that a large fraction of particles above 100 nm in the PM2.5 fraction is due to agglomerated ultrafine particles, primarily from the combustion related sources. Thus, in urban areas, about 1/3 of the average PM2.5 level at about 18-20 μg/m^3 is due to these combustion related fractions.

Therefore, it can be assumed that about 30% of the overall PM2.5 exposure may be due to free + agglomerated ultrafine particles. This would equal an average exposure to ultrafine particles or agglomerates thereof of about 5-6 μg/m^3.

Assuming a daily ventilation rate of 20 m^3 for an ***adult person*** in urban environments, this would lead to a daily exposure to 100-120 μg/day. For an adult person of 70 kg, a daily inhalational dose can be estimated to ***1.4- 1.7 μg /kg bodyweight/day***.

Thus ***children*** (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to ***2.5-3 µg /kg bodyweight/day***.

Effects and dose response relationship

In a newly published report, an overall health impact assessment of the air pollution in Denmark has been made. The following table shows the most severe health outcomes based on the levels of PM2.5 in Denmark. The data are based on PM2.5 exposure modelling made for the entire Danish population and dose-response relationships for the PM2.5 exposure and the adverse health outcomes.

ESTIMATED NUMBER OF VARIOUS NEGATIVE HEALTH OUTCOMES IN DENMARK (2011) DUE TO MAINLY AMBIENT PM2.5 EXPOSURE OF THE POPULATION (DCE 2014)

Adverse health effects	Number of cases -estimations for 2011-
Mortality, acute exposure	142
Mortility, long term exposure	3 330
Years of life lost (YOLL)	35 300
Infant mortality	4
Cardiac failure	285
Hospital admissions, Cerebro-vascular diseases	416
Lung cancer	506
Chronic bronchitis	3 300
Hospital admissions, Respiratory diseases	179
Days with reduced activity (sickness days)	3 380 000

As indicated in the table, there is substantial negative health effects associated with ambient PM2.5. Thus, the estimated mortality of 3 330 people in 2011 contributes with more than 5% of the total mortality in Denmark.

There is a general consensus in literature that the toxicity of PM2.5 to a great extent is driven by the combustion related constituents (e.g. from traffic exhaust and wood burning) and that the combustion related fraction of PM2.5 is more potent in relation to adverse health outcomes compared to the remaining fractions in PM2.5 of mineral origin. Thus, larger dose-response relationships have been found in areas where the PM2.5 content in air was dominated by traffic exhaust or wood burning, and also several data indicate increased dose-response relationship for people living close to roads with dense and heavy traffic. When mass based measurements have been made for elemental carbon or black carbon studies indicate an up to ten times higher potency for these measures compared to the associations to the health based effects for PM2.5. However, more precise and *independent* dose-response relationships for the combustion derived and ultrafine derived fractions are still to be determined.

Thus, it may be assumed that at least the same dose-response relationship (on weight basis) as found for PM2.5 applies for ultrafine particles. If it is assumed that 1/3 of the PM2.5 levels pertain

to ultrafine particles (free+ agglomerated) this indicates that the ultrafine particles (free + agglomerated) account for at least 1/3 of the adverse health outcome as indicated in the above table.

Ultrafine particles in indoor air

Sources and particle levels in indoor air

Several studies have used mobile devices for measuring ultrafine particles and particle numbers in the indoor environment. In these studies, the levels are measured in different locations in different situations and during different indoor activities.
In a study in 56 Danish homes, Bekö et al. (2013) reported a geometric mean of *22.3 x 10^3 particles/cm^3* during the period when the occupants were awake. During sleep and when the homes were vacant the mean levels were below 6.1 x 10^3 particles/cm^3.

A very high variation in the 24-hour average levels was found among the 56 homes, ranging from about 1.5 x 10^3 particles/cm^3 to 2.5 x 10^5 particles /cm^3 for the geometric means. At the high exposure levels, 97% of the particles originated from the use of candles.

The overall average mean for the integrated 24 hour exposure was calculated to 334 x 10^3 particles (hour /cm^3 day). The average particle diameter was found to be 76 nm with only 5% of the measured particles above 120 nm.

Test chamber investigations have demonstrated that the highest emission levels were achieved in relation to candle burning, whereas using a radiator, cigarette smoking and frying meat also contributed with very high levels (all above 150 x 10^3 particles/cm^3).

Data from wood burning in Danish homes indicate indoor levels of ultrafine particles in the range of 5 x 10^3 to 2 x 10^5 particles/cm^3.

All these various indoor sources explain the high variation of indoor measurements and also further underpin the importance of the indoor environment for the overall daily exposure to ultrafine particles.

Exposure to indoor ultrafine particles

From the above, it is evident that the personal exposure to ultrafine particles due to many hours spent in the home, would very much depend on which types of activities and indoor sources are present in the home.

From measurements in 56 Danish homes, Bekö et al. (2013) found an overall mean 24 hour exposure level *15 600 particles/cm^3* and a mean integrated 24-hours exposure level of 334 x 10^3 particles (hour/cm^3 day).

Thus, for ***an adult person*** inhaling 20m^3 per day, this would result in a daily inhalation of ***2.8 x 10^{11} particles/day*** or about ***4 x 10^9 particles/kg bodyweight/day*** for a person weighing 70 kg.

Small children (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to ***7 x 10^9 particles kg bodyweight/day.***

The composition of the various fractions of the ultrafine particle exposure may vary a lot depending of the source. However, very little has been found on measurements of the chemical characterisation of the indoor ultrafine particles.

With respect to a *mass based exposure estimate* to ultrafine particles + agglomerates thereof, an estimate may be based on typical indoor PM2.5 levels of 20-30 µg/m^3 as indicated from data from German homes. If it is assumed –as for the ambient air particles - that 1/3 of this PM2.5 level stems from ultrafine + agglomerated ultrafine particles, this would correspond to an exposure level of 7-10 µg/m^3.

If an ***adult person*** daily inhales 20 m^3 air, this would result in a daily exposure of 140-200 µg/m^3 of ultrafine particles. With a bodyweight of 70 kg this would correspond to ***2-3 µg/kg bodyweight/day.***

Small children (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to ***3.5-5 µg/kg bodyweight/day.***

Effects and dose response relationship
In general there is a very sparse data base on adverse health effects related to the levels of ultrafine particles or PM2.5 in a typical home. Hazard and risk assessment of indoor air particulate matter is therefore at present based on the data from particulate matter in ambient air, as particles in ambient air also significantly contribute to the indoor air.

Recently, the Norwegian Folkehelseinstituttet has made a review on indoor air pollutants including particulate matter in order to make recommendations with respect to guideline values for these pollutants. It was acknowledged that the data base on the adverse effects on indoor particles is very poor both in relation to PM2.5 and in relation to data on the health implication of ultrafine particles. Therefore, they based their assessment of particles in indoor air on the data base on PM2.5 and the WHO evaluations on particles in ambient air.

It should be emphasised that various sources exist for ultrafine particles in indoor environments as described above and that exposure from these sources may exceed the exposure to particles in ambient air. Thus, for a proper risk assessment of the indoor sources, data are urgently needed in order to characterise these particles both in terms of physical-chemical properties and in terms of their hazards.

Ultrafine particles (nanomaterials) in drinking water and soil
Very little data are available regarding measured levels of nanoparticles/nanomaterials in environmental matrices including drinking water and soil. This is partly due to the general lack of suitable analytical methods (including sample preparation techniques) that are sensitive and selective enough to identify and quantify nanoparticles in relevant concentrations, partly due to the complex nature of most environmental matrices and the environmental transformation processes changing the character of the nanoparticle to be studied. Furthermore, it is very difficult with the current analytical methods to distinguish between nanoparticles of anthropogenic origin ("engineered" nanoparticles) and nanoparticles of natural origin.

Thus, no relevant measurements of nanoparticles in drinking water or soil could be found in relation to this project and only a few scattered data on the occurrence in surface water (a potential source of drinking water). The only more systematic data reflecting environmental levels of a number of nanoparticles in water and soil were found in six studies providing modelled predictions. However, these estimates are considered to be associated with very high uncertainty as they varied orders of magnitude for a specific nanomaterial.

From this, it was concluded that the existing data was too poor to form a basis for any meaningful estimates regarding human exposure to nanomaterials through drinking water and soil.

Ultrafine particles (nanomaterials) in consumer products

In another part of this project the exposure to nanomaterials from the use of selected consumer products have been estimated. Both exposure estimates in relation to oral, dermal, inhalational and eye exposure were made whatever considered most relevant for the specific product.

When assessing exposure to nanoparticles from environment and from consumer products comparison can only be made for the inhalational exposure route, as no estimates on oral and dermal exposure from environmental media has been made.

The estimated consumer exposure to nanoparticles from these products are given in the below table.

Comparison of exposure to ultrafine particles from various sources

A direct comparison between the exposure levels and exposure estimates that have been made may be difficult due to different methods and conditions for the measurements (e.g. different time scales). However, a cautious attempt for evaluating the exposure impact of the various sources and locations can be made from a compilation of the exposure estimates in the following table:

Exposure levels of ultrafine particles			
	Particle no/cm^3	mg/m^3	µg/kg/day
Environmental 24-hours exposure levels			
Ambient air, annual average	4 x 10^3 - 15 x 10^3	0.005 - 0.006	1.4 - 1.7
Indoor air Range 24-hours Average 24-hours	(1.5 – 250) x 10^3 – 14 x 10^3	0.007 - 0.010	2 - 3
Person borne measurement (integrated exposure) average 24-hours non-smokers	(9.2-29) x 10^3	-	-
Use of products -estimated exposure levels -			
Face powder 15 min	>10 x 10^3	0.26	0.9
Paint sanding 30 min	-	18	220
Paint spraying 30 min	-	109	1300
Surface coating 30 min	-	0.0021	0.02
Pump spray 10 min	(3.4 – 6) x 10^3	0.0043	0.017
Cement Handling 8 hours Grinding 8 hours	- -	0.25 0.75	42 130
Indoor sources - measured exposure levels -			
Frying meat	151 x 10^3	-	-
Electric stove	112 x 10^3	-	-
Gas stove	80 x 10^3	-	-
Radiator	218 x 10^3		
Vacuum cleaning	(21-38) x 10^3	-	-
Candle burning	(70 – 242) x 10^3	-	-

Exposure levels of ultrafine particles			
	Particle no/cm^3	mg/m^3	µg/kg/day
Cigarette	213 x 10^3	-	-

Particle number concentrations (particle no/cm^3)
In the table only a selection of indoor sources is presented. However, the very high number concentrations that have been measured for various indoor sources support that the 24-hours measurements in indoor environment are very much impacted by these sources. Also, the personal borne measurements data indicate that the highest daily number based exposure to ultrafine particles comes from the indoor environment and the indoor sources.

Data on particle number concentrations from use of consumer nano-products are sparse. The present data in relation to face powder and pump spray indicate, however considerable lower exposure levels compared to many other indoor sources. Furthermore, the exposure to the particles from face powder is very short (less than 15 minutes per day). This may also apply to other consumer product e.g. sprays that are often used only a couple of minutes.

Mass based concentrations (mg/m^3 and µg/kg bodyweight/day)
Very few PM0.1 measurements are available for evaluating the mass based exposure to free ultrafine particles in the air. Thus the mass based concentrations estimated here include the exposure estimate for both free and agglomerated ultrafine particles.

In relation to the exposure levels from the products these have been made based on the fraction of nanomaterial used in the product. It is, however, especially for the paint spraying and paint sanding scenarios due to the binding of the nanomaterial in a liquid or dried matrix, very uncertain to which extent this exposure actually reflect exposure to nanomaterials.

For other product scenarios, such as face powder and cement handling and grinding, considerable higher mass based concentrations may be reached compared to ambient and indoor levels. It should be noticed that the average daily exposure (expressed in µg/kg bodyweight/day) for face powder is nearly at the level of the environmental exposure, whereas the daily exposure from cement handling and grinding is considerably higher.

The estimated exposure level to nanomaterials of 0.004 mg/m3 from pump spray containing 1% of nanomaterial is not considered to exceed the environmental levels of ultrafine particles. Thus the daily exposure from a pump spray used in 10 minutes is in this case estimated to result in a daily exposure of 2 orders of magnitudes lower than the environmental exposures (expressed in µg/kg bodyweight/day).

Comparison of risk
Ambient air
Adverse health effects have been attributed to the content of ultrafine particles (free plus agglomerated particles) in the ambient air especially in relation to long-term exposure where increased mortality is the most prominent finding. From the data on PM2.5 in ambient air, it may be assumed that an annual exposure level of 1 µg/m^3 of ultrafine particles (free plus agglomerated particles) is associated with an increase in mortality of at least 0.6%. This may be put into perspective as the current annual levels of free plus agglomerated ultrafine particles in Denmark is assumed to be in the range of 5-6 µg/m^3.

Indoor Air
Due to many indoor emission sources of ultrafine particles, the levels of free ultrafine particles as well as the levels of free plus agglomerated ultrafine particles are considered higher than the ambient exposure.

However, data on the human health hazards in relation to indoor particle levels is very poor and at present often the same dose-response relationship as for the ambient air particles is used. However, it should be emphasised that great uncertainties applies to this approach.

Consumer nano-products

Even less data than for indoor particles are available in relation to the human health hazard from the nanomaterial exposure from the use of nano-products.

Even though data on ultrafine particle in ambient air call for concern in relation to exposure from manufactured nanomaterials/nanoparticles, it cannot be recommended to extrapolate risk from data on ambient air particles as the composition of the particles from nano-consumer products is quite different from the composition of ambient air particles. Thus, the use of such an approach would be based on pure guesswork rather than be substantiated by sound scientific argumentation.

In conclusion and in relation to nanomaterial exposure from consumer product, the most appropriate approach at present time for risk assessment is a case-by-case approach and using data on actual exposure levels and hazard data on the specific nanomaterials. Although both exposure data and hazard data to a great extent are lacking for many nanomaterials, increased research efforts within the latest decade now begin to provide new information and a better understanding of nano-specific properties, so that the basis for more detailed risk assessments is growing and will further grow in the coming years.

Sammenfatning og konklusion

Under overskriften "Bedre styr på nanomaterialer" har den danske Miljøstyrelse iværksat en række projekter, der sigter på at undersøge og generere ny viden om forekomsten af nanomaterialer i produkter på det danske marked og vurdere potentielle risici for forbrugerne og miljøet.

Denne rapport er en del af en serie på fire i et projekt, som omhandler forbrugereksponering og risikovurdering af nanomaterialer i produkter på det danske marked.

Målet med denne rapport er imidlertid at vurdere befolkningens eksponering for nanopartikler fra miljøet, dvs. fra udeluft, indeluft, og fra jord og vand (drikkevand), samt at beskrive den risiko, der er forbundet med denne eksponering. Disse data skal være med til at perspektivere de mulige risici, der er forbundet ved eksponering for nanomaterialer fra anvendelse af forbruger-nanoprodukter, som beskrevet i andre dele/arbejdspakker i dette projekt.

Denne rapport opsummerer den aktuelle viden om risikoen for befolkningen i forbindelse med udsættelse for nanopartikler fra miljøet og omfatter:

- Opsummering af viden fra oversigtsrapporter mht. befolkningens eksponering og risiko for nanopartikler fra udstødning i trafikken og andre kilder, fx indeluftens partikelforurening
- Opsummering af viden om tilstedeværelse af nanopartikler i drikkevand og jord og vurdering af befolkningens eksponering for nanopartikler fra disse kilder.

Ultrafine partikler i udeluften
I udeluft omtales nanopartikler generelt som ultrafine partikler, hvor ultrafine partikler er defineret som partikler mindre end 100 nm i diameter. Forhøjede niveauer af ultrafine partikler i udeluften stammer hovedsageligt fra forbrændingsprocesser, fx trafikudstødning og brændeovnsrøg.

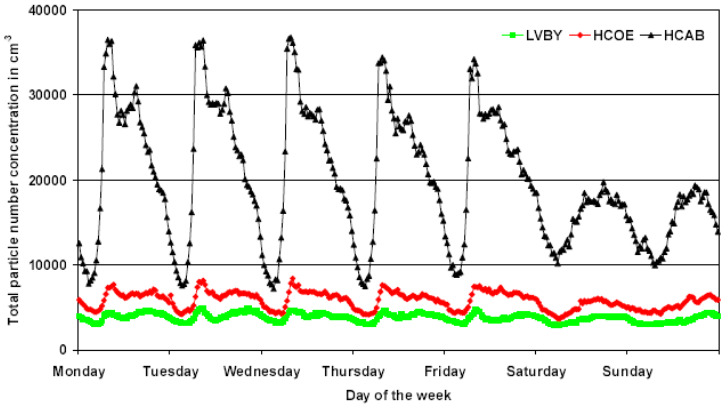
Befolkningsundersøgelser viser, at måling af PM2,5 (partikler i mg/m^3 med en diameter under 2,5 µm) generelt er den måleenhed, der er bedst korreleret til de sundhedsskadelige effekter fra udeluften. Sammenhængen mellem PM2,5 (også kaldet fine partikler) og sundhedsmæssige risici har medført, at der også er kommet fokus på mindre størrelsesfraktioner, herunder de ultrafine partikler. De ultrafine partikler kan enten måles på vægtbasis, angivet som PM0,1 i mg/m^3, eller de kan måles på basis af antal (i enheden antal partikler/cm^3). På grund af de ultrafine partiklers ringe vægt bidrager de (målt som PM0,1) kun lidt til den samlede masse af partikler målt i mg/m^3, når der måles for de større partikelfraktioner i PM2,5 og især PM10 (vægten af partikler op til 10 µm i diameter).

Da ultrafine partikler er meget ustabile i luft (som følge af hurtig agglomerering til større partikler), er der meget høj variation af indholdet af frie ultrafine partikler selv inden for korte afstande. Således falder koncentrationerne af ultrafine partikler meget hurtigt med stigende afstande fra emissionskilderne, fx trafikerede veje og brændeovne Dette betyder, at niveauerne af ultrafine partikler ofte varierer betydeligt fra ét sted til et andet inden for samme by/nærområde.
Derfor vil eksponeringsvurderinger for befolkningen for ultrafine partikler baseret på data fra fast placerede målestationer være behæftet med meget stor usikkerhed sammenlignet med eksponeringsvurderinger for PM2,5 og PM10, hvor de målte niveauer i langt højere grad repræsenterer befolkningens eksponering.

På et givent sted i en by vil antallet af ultrafine partikler imidlertid typisk udvise et ensartet mønster mht. stigende og faldende niveauer i løbet af en dag.

Niveauer af ultrafine partikler i luften

At der i byluft kan forekomme store variationer i antallet af ultrafine partikler hen over en dag og på forskellige lokaliteter kan illustreres ved nedenstående figur, der viser udsvingene af ultrafine partikler på en trafikeret vej i København (HCAB op til 36 000-37 000 partikler/cm^3), i bybaggrund i København (HCOE op til omkring 8000 partikler/cm^3) samt baggrundsniveauet på landet (LVBY op til omkring 5000 partikler/cm^3) (DMU 2011).



DAGSVARIATION AF ANTALLET AF ULTRAFINE PARTIKLER. (NERI 2011). SORT KURVE: TRAFIKERET GADE. RØD KURVE: BYBAGGRUND. GRØN KURVE: LANDBAGGRUND.

I 2011 blev det gennemsnitlige *årlige* baggrundsniveau for et landområde målt til omkring 4 000 ultrafine partikler pr. cm^3. Luften i bybaggrunden i København indeholdt yderligere ca. 2 000 partikler pr. cm^3, mens en trafikeret gade i København indeholdt yderligere 11 000 til 14 000 partikler pr. cm^3 i forhold til landbaggrundsniveauet.

I 2011 var gennemsnitsniveauet af PM2,5 i København (ved en trafikeret gade) ca. 20 µg/m^3, med et gennemsnitligt partikelantal på ca. 15 000 partikler/cm^3. På landet måltes et baggrundsniveau for PM2,5 på 15 µg/m^3 og et partikelantal på 4 000 partikler/cm^3.

Kilder og sammensætning

NERI (2011) angiver følgende kilder som særligt betydende for niveauerne af ultrafine partikler i udeluften:

-Forbrænding af biobrændstof (boligopvarmning med træ, skovbrande osv.)
-Olieforbrænding
-Kulforbrænding
-Kørende trafik
-Samt sekundære organiske partikler dannet ved iltning af af VOC'er og semi-VOC'er (fordampelige organisk-kemiske forbindelser)

Med hensyn til andre kilder, fx *uorganiske salte* og *mineralske partikler*, er det meget usikkert, hvor meget de bidrager til niveauet af ultrafine partikler i luften.

Der er ikke foretaget konkrete vurderinger af de forskellige emissionskilder og deres relative bidrag til emissionen af ultrafine partikler i Danmark. For de årlige danske emissioner af PM2,5 derimod, er der for 2005 vurderet følgende fordeling af emissionerne (DMU 2009):

-Trafikudstødning: 13% af PM2,5 emissionerne (ca. 3 500 tons PM2.5)
-Boligopvarmning med træ: 64% af PM2,5 emissionerne (ca. 17 000 tons PM2.5)
-Anden forbrænding: 14% af PM2,5 emissioner (ca. 3 700 tons PM2.5)

Det må imidlertid forventes, at en meget stor massebaseret fraktion af disse forbrændingsrelaterede kilder udledes som ultrafine partikler, som efter kort tid i luften agglomererer/aggregerer til større partikler. De ultrafine partikler fra forbrænding består hovedsageligt af rent kulstof, sod og organisk bundet kulstof. Partikler med organisk bundet kulstof er partikler, der dannes fra gasser af flygtige organiske kulstof forbindelser (biogene eller antropogene), som reagerer med atmosfæriske oxidanter fx O_3, NO_3 eller OH og dermed danner partikler (NERI 2011). Niveauerne for disse forbrændingsfraktioner kan enten afspejles i målinger af partikelantal (måling af frie ultrafine partikler) eller i vægtbaserede parametre såsom sorte partikler (black smoke), sod, elementært (rent) kulstof eller organisk kulstof.

Generelt bidrager forbrændingsfraktionerne med 25-33% af PM2,5-indholdet i luften for henholdsvis baggrundsniveauer og for gadestationer i byer.

Eksponering for ultrafine partikler
Som angivet i ovenstående figur er de gennemsnitlige årlige eksponeringsniveauer for ultrafine partikler i Danmark i størrelsesordenen 4 000 til 15 000 partikler/cm^3 for bybaggrund, henholdsvis trafikerede gader. (M.h.t. kortvarige spidskoncentrationer er der målt niveauer op til 180 000 ultrafine partikler/cm^3 ved særlige "hot spot"-steder med kraftig trafik).

For en ***voksen person*** , der vejer 70 kg og indånder 20m^3 luft per dag, vil disse niveauer således medføre en gennemsnitlig daglig eksponering på 8-30 x 10^{10} partikler pr. dag, eller ***1-4 x 10^9 partikler/kg legemsvægt/dag***.

For ***små børn*** er eksponeringen højere, da de i forhold til deres kropsvægt indånder mere luft end voksne. Små børn (1-5 år gamle), der indånder 0,5 m^3/kg legemsvægt/dag, vil således blive eksponeret for ***2 – 7,5 x 10^9 partikler/kg legemsvægt/dag.***

Det skal dog bemærkes, at disse eksponeringstal kun indikerer eksponeringsniveauet for eksponering for frie ultrafine partikler, og at en stor fraktion af partikler over 100 nm i PM2,5-fraktionen udgøres af agglomererede ultrafine partikler, primært fra forbrændingsrelaterede kilder. I byområder udgør forbrændingspartikler ca.1/3 af det gennemsnitlige PM2,5-niveau på omkring 18-20 µg/m^3. Det kan derfor antages at ca. 30% af den samlede PM2,5-eksponering kan relateres til frie + agglomererede ultrafine partikler. Dette ville svare til en gennemsnitlig eksponering for ultrafine partikler eller agglomerater heraf på ca. 5-6 µg/m^3.

For en ***voksen person***, der vejer 70 kg og indånder 20m^3 luft per dag, vil dette således medføre en gennemsnitlig daglig eksponering på 100-120 µg/dag, eller til ***1,4-1,7 µg/kg legemsvægt/dag***

Børn (1-5 år gamle), der indånder 0,5 m^3/kg/dag, bliver tilsvarende eksponeret for ***2,5-3 µg/kg legemsvægt/dag***.

Effekter og dosis-respons sammenhænge
I en nyligt offentliggjort rapport (DCE 2014) er der foretaget en samlet vurdering af de sundhedsskadelige effekter af luftforureningen i Danmark. Nedenstående tabel viser de mest alvorlige sundhedsmæssige effekter knyttet til PM2,5 eksponeringen i Danmark. Data er baseret på PM2,5 eksponeringsmodellering foretaget for hele den danske befolkning samt de seneste dosis-respons sammenhænge for PM2,5-eksponering og sundhedsskadelige effekter.

OMFANG AF SUNDHEDSSKADELIGE EFFEKTER I BEFOLKNINGEN I DANMARK, PRIMÆRT SOM FØLGE AF PM2,5-EKSPONERINGEN (DCE 2014)

Sundhedsskadelige effekter	Antal tilfælde -skøn for 2011-
Dødsfald, akut eksponering	142
Dødsfald, langtidseksponering	3 330
Tabte leveår (YOLL)	35 300
Børnedødsfald	4
Hjertesvigt	285
Hospitalsindlæggelser, Blodkarsygdomme i hjernen	416
Lungecancer	506
Kronisk bronkitis	3 300
Hospitalsindlæggelser, Luftvejssygdomme	179
Dage med nedsat aktivitet (sygedage)	3 380 000

Som det fremgår af tabellen, er der betydelige sundhedsskadelige effekter forbundet med indholdet af PM2,5 i udeluften. Således bidrager de anslåede årlige dødsfald på 3330 mennesker med mere end 5% af den samlede dødelighed i Danmark.

Der er generel enighed blandt de internationale ekspertvurderinger, at toksiciteten af PM2,5 i stor udstrækning kommer fra de forbrændingsrelaterede bestanddele (fx udstødning fra trafikken og brænderøg), og at den forbrændingsrelaterede del af PM2,5 har kraftigere effekt i forhold til det øvrige indhold i PM2,5 (fx af mineralsk oprindelse). Således er der fundet tydeligere og kraftigere dosis-respons sammenhænge i områder, hvor PM2,5-indholdet i luften var domineret af udstødning fra trafikken eller brænderøg, og i områder med stærkt trafikerede veje og tung trafik. Når der er foretaget vægtbaserede målinger for rent kulstof eller sorte partikler (black smoke), tyder undersøgelser på en op til ti gange højere potens for disse komponenter i forhold til sammenhængen med PM2,5. Det er dog svært at adskille og underopdele effekterne for de forskellige komponenter i PM2,5, og der savnes fortsat mere præcise og *uafhængige* dosis-respons sammenhænge for forbrændingsfraktionerne, herunder de ultrafine partikler.

Det kan på baggrund af ovenstående antages, at mindst tilsvarende dosis-respons forhold (på vægtbasis) som fundet for PM2,5 gælder for forbrændingsfraktionen og de ultrafine partikler heri. Hvis det antages, at 1/3 af PM2,5-niveauerne udgøres af ultrafine partikler (frie + agglomererede), indikerer dette, at de ultrafine partikler (frie + agglomererede) tegner sig for mindst 1/3 af de sundhedsskadelige effekter, som angivet i ovenstående tabel.

Ultrafine partikler i indeklimaet

Kilder og partikelniveauer i indeluft

Adskillige undersøgelser har anvendt transportabelt måleudstyr til måling af ultrafine partikler og partikelantal i indeklimaet. I disse undersøgelser er partikelniveauerne målt på forskellige lokaliteter, i forskellige situationer og under forskellige indendørs aktiviteter.

I en undersøgelse omfattende 56 danske boliger rapporterede Bekö et al (2013) et gennemsnit (geometrisk) på 22,3 x 10^3 partikler/cm^3 i det tidsrum, hvor beboerne ikke sov. Under søvn og når ingen var hjemme, var de gennemsnitlige niveauer under 6,1 x 10^3 partikler/cm^3.

Der blev fundet meget stor variation i de gennemsnitlige 24 timers niveauer i de 56 boliger, lige fra ca. 1,5 x 10^3 partikler/cm^3 til 2,5 x 10^5 partikler/cm^3 for de geometriske middelværdier. Ved de meget høje niveauer stammede 97% af partiklerne fra brug af stearinlys.

Den gennemsnitlige partikeldiameter var på 76 nm med kun 5% af de målte partikler over 120 nm. Den gennemsnitlige middelværdi for den integrerede 24 timers eksponering blev for målingerne beregnet til 334 x 10^3 partikler (timer/cm^3/dag).

Også undersøgelser i testkammer har vist, at de højeste niveauer blev opnået i forbindelse med afbrænding af lys, men brug af radiatorer, cigaretrygning og stegning af kød bidrog også med meget høje niveauer (alle over 150 x 10^3 partikler/cm^3).

Data i forbindelse med brændeovnsfyring i danske boliger har vist indendørs niveauer af ultrafine partikler i området 5 x 10^3 til 2 x 10^5 partikler/cm^3.

De mange forskellige indendørs kilder forklarer den høje variation af indendørs målinger og understreger også betydningen af indeklimaet for den samlede daglige eksponering med (frie) ultrafine partikler.

Eksponering for ultrafine partikler i indeluft
Ud fra ovenstående står det klart, at den personlige eksponering for ultrafine partikler på grund af de mange timer, der tilbringes i boligen, vil afhænge meget af, hvilke typer aktiviteter og indendørs kilder, der er til stede i boligen.

Ud fra målinger i 56 danske boliger fandt Bekö et al. (2013) et samlet gennemsnitligt 24-timers eksponeringsniveau på 15 600 partikler/cm^3 og et gennemsnitligt integreret 24-timers eksponeringsniveau på 334 x 10^3 partikler (timer/cm^3 dag).

Dette vil for en ***voksen person***, der vejer 70 kg og som indånder 20 m^3 pr. dag, resultere i en daglig indånding af ***2,8 x 10^{11} partikler/dag*** eller omkring ***4 x 10^9 partikler/kg legemsvægt/dag.***

Små børn (1-5 år gamle), der indånder 0,5 m^3/kg/dag, vil tilsvarende blive eksponeret for ***7 x 10^9 partikler kg legemsvægt/dag.***

Sammensætningen af de forskellige fraktioner af ultrafine partikler i indeluft kan variere meget afhængigt af kilden. Imidlertid er der blevet fundet meget få data med hensyn til den kemiske sammensætning af de ultrafine partikler i indeluften.

Med hensyn til en vægtbaseret eksponeringsvurdering for ultrafine partikler + agglomerater heraf kan en vurdering baseres på typiske indendørs PM2,5-niveauer på 20-30 µg/m^3 (målinger fra tyske boliger). Hvis det - som for udeluftspartikler – antages, at 1/3 af dette PM2,5-niveau stammer fra ultrafine + agglomererede ultrafine partikler, vil dette svare til et eksponeringsniveau på 7-10 µg/m^3.

Dette vil for en ***voksen person,*** der dagligt indånder 20 m^3 luft, resultere i en daglig eksponering på 140-200 µg/m^3 ultrafine partikler. Med en kropsvægt på 70 kg svarer dette til ***2-3 µg/kg legemsvægt/dag.***

Små børn (1-5 år gamle), der indånder 0,5 m^3/kg/dag, vil tilsvarende blive eksponeret for ***3,5-5 µg/kg legemsvægt/dag.***

Effekter og dosis-respons sammenhænge
Der er generelt meget få data, der beskriver sundhedsskadelige effekter af partikler i indeklimaet. Fare- og risikovurdering af indeluftspartikler er derfor i øjeblikket baseret på data fra partikler i udeluft, som imidlertid også kan bidrage væsentligt til partikelniveauet indendørs.

Det norske Folkehelseinstitut har i 2013 foretaget en vurdering af luftforurening i indeklimaet, herunder partikler, for at udarbejde vejledende værdier for indhold i luften. Det blev i denne sammenhæng vurderet, at viden om effekterne af partikler i indeklimaet er meget sparsomme både i forhold til PM2,5 og i forhold til data vedrørende ultrafine partikler. Derfor baserede Folkehelseinstituttet deres vurdering af partikler i indeluft på WHO´s vurderinger af PM2,5 i udeluft.

Det skal understreges, at der findes mange forskellige kilder til ultrafine partikler i indeluften, og at eksponering fra disse kilder typisk vil overstige eksponering for ultrafine partikler i udeluften. Derfor er der et stort behov for bedre at karakterisere disse partikler både med hensyn til fysisk-kemiske egenskaber og sundhedsskadelige effekter for at kunne foretage mere præcise risikovurderinger af kilderne til partikelforureningen i indeklimaet.

Ultrafine partikler (nanomaterialer) i jord og drikkevand.
Der er meget få data til rådighed vedrørende til målte niveauer af nanopartikler/nanomaterialer i miljøet, herunder grundvand, drikkevand og jord. Dette skyldes til dels en generel mangel på egnede analysemetoder (herunder prøveoparbejdning), der er følsomme og selektive nok til at identificere og kvantificere nanopartikler i relevante koncentrationer. Dette skyldes den komplekse karakter af prøvernes sammensætning samt de miljømæssige omdannelsesprocesser, som kan ændre karakteren af de nanopartikler, der ønskes bestemt. Desuden er det meget svært med de nuværende analysemetoder at skelne mellem nanopartikler af antropogen oprindelse (dvs. industrielt forarbejdede nanopartikler) og nanopartikler af naturlig oprindelse.

I forbindelse med dette projekt har det således ikke været muligt at finde relevante målinger af nanopartikler i drikkevand eller jord, mens der kun foreligger få og spredte data om forekomst i overfladevand (en potentiel kilde til drikkevand). De eneste systematiske data, der afspejler miljømæssige niveauer af en række forskellige nanopartikler i vand og jord, er fundet i seks undersøgelser med modelberegnede niveauer. Disse vurderinger vurderes imidlertid at være forbundet med meget stor usikkerhed, da de estimerede niveauer i nogle tilfælde varierer med flere størrelsesordener for et specifikt nanomateriale.

På den baggrund konkluderes det, at de eksisterende data endnu er for sparsomme til at kunne danne grundlag for meningsfyldte vurderinger af human eksponering for nanomaterialer via drikkevand og jord.

Ultrafine partikler (nanomaterialer) i forbrugerprodukter
I en anden del af dette projekt blev befolkningens (forbrugerens) eksponering for nanomaterialer estimeret ud fra anvendelse af en række udvalgte forbrugerprodukter. Der blev udført eksponeringsvurdering både i relation til oral indtagelse, hudkontakt, indånding og øjenkontakt, alt efter, hvad der ansås for at være mest relevant for det specifikke produkt.

Når eksponering for nanopartikler fra miljøet og eksponering med nanomaterialer fra forbrugerprodukter skal sammenlignes kan denne sammenligning kun baseres på eksponering via indånding, da der ikke haves data for oral og dermal eksponering fra miljøet.

I nedenstående tabel angives dels eksponeringen med nanopartikler gennem udeluft og indeklimaet og dels eksponeringen fra udvalgte forbrugerprodukter.

Det kan imidlertid være vanskeligt at foretage en direkte sammenligning mellem værdierne for eksponeringsniveauerne, på grund af forskellige metoder og betingelser for målingerne og beregningerne (fx forskellige tidsskalaer).

Sammenligning af eksponering for ultrafine partikler fra diverse kilder

Eksponeringsniveauer for ultrafine partikler			
Miljømæssige eksponeringer			
	Partikelantal/cm³	**mg/m³**	**µg/kg/dag**
Udeluft Årligt gennemsnit	4×10^3 - 15×10^3	0.005 - 0.006	1.4 - 1.7
Indeluft Min-max over 24 timer Gennemsnit 24 timer	$1.5 \times 10^3 – 2.5 \times 10^5$ 14×10^3	0.007 - 0.010	2 - 3
Personbårne målinger Gennemsnit 24 timer ikke-rygere	$9.2\text{-}29 \times 10^3$	-	-
Eksponeringsniveau fra brug af produkter			
Ansigtspudder 15 min	$>10 \times 10^3$	0.26	0.9
Slibning af maling 30 min	-	18	220
Sprøjtemaling 30 min	-	109	1300
Overfladebehandling, aerosol spray 30 min	-	0.0021	0.02
Overfladebehandling, Pumpespray, 10 min	$(3.4 – 6) \times 10^3$	0.0043	0.017
Cement Håndtering 8 timer Afslibning 8 timer	- -	0.25 0.75	42 130
Indeklima kilder, ekponeringsniveauer			
Stegning af kød	15×10^4	-	-
Elektrisk komfur	11×10^4	-	-
Gaskomfur	8×10^4	-	-
Radiator	22×10^4		
Støvsugning	$(2.1\text{-}3.8) \times 10^4$	-	-
Stearinlys	$(7 – 24) \times 10^4$	-	-
Cigaret	21×10^4	-	-

Partikelantal (partikelantal/cm³)
I tabellen præsenteres kun et udvalg af indendørs kilder. De meget høje niveauer, der er målt for forskellige indendørs kilder, anskueliggør, at 24-timers målingerne i indeklimaet er meget påvirkede af disse kilder. De personbårne målinger indikerer endvidere, at indeklimaet og dets kilder leverer hovedbidraget til den daglige eksponering for ultrafine partikler.

Data m.h.t. partikelantal i forbindelse med brug af nano-forbrugerprodukter er fortsat meget sparsomme. De foreliggende data i relation til ansigtspudder og pumpespray tyder dog på betydeligt

lavere eksponeringsniveauer i forhold til mange andre indendørs kilder. Endvidere er eksponeringen for partiklerne fra fx ansigtspudder meget kortvarig (mindre end 15 minutter om dagen). Dette kan også gælde for andre forbrugerprodukter, fx spray, der ofte kun anvendes et par minutter.

Massebaserede koncentrationer (mg/m³ og µg/kg legemsvægt/dag)
Der er meget få PM0,1-målinger tilgængelige for evaluering af massebaseret eksponering for frie ultrafine partikler i luften. Således omfatter de massebaserede estimerede koncentrationer, som angivet i tabellen, summen af frie og agglomererede ultrafine partikler.

Eksponeringsniveauerne for produkterne er foretaget på basis af den fraktion af nanomaterialet, der er indeholdt i produktet, og ikke på forekomsten af frie nanopartikler. Det er således meget usikkert, især for sprøjtemalings- og slibningsscenarierne, i hvilket omfang denne eksponering faktisk afspejler eksponeringen for et nanomateriale, da nanomaterialet kan være fast bundet i en flydende eller indtørret matrix.

For andre produktscenarier, såsom ansigtspudder og håndtering/afslibning af cement, kan der opnås betydeligt højere massebaserede koncentrationer i forhold til de udendørs og indendørs niveauer. Det skal bemærkes, at den gennemsnitlige daglige eksponering (udtrykt i µg/kg legemsvægt/dag) for ansigtspudder næsten er på niveau med den miljømæssige eksponering, mens den daglige eksponering fra håndtering og afslibning af cement er betydeligt højere.

Det estimerede eksponeringsniveau for nanomaterialer på 0,004 mg/m³ fra pumpespray indeholdende 1% nanomateriale vurderes derimod ikke at være højere end de miljømæssige niveauer af ultrafine partikler. Således estimeres den daglige eksponering fra en pumpespray ved en anvendelsestid på 10 minutter, i dette tilfælde at resultere i en daglig eksponering på 2 størrelsesordener lavere end de miljømæssige eksponeringer (udtrykt i µg/kg legemsvægt/dag).

Sammenligning af risiko
Udeluft
Indholdet af ultrafine partikler (frie plus agglomererede partikler) i udeluften tilskrives betydelige sundhedsskadelige effekter, især i forhold til langvarig eksponering, hvor øget dødelighed udgør den mest markante effekt. Fra data for PM2,5 i udendørs luft må det antages, at et årligt eksponeringsniveau på 1 µg/m³ ultrafine partikler (frie plus agglomererede partikler) som minimum er forbundet med en stigning i dødeligheden på 0,6%. Dette skal ses i sammenhæng med at de nuværende årlige niveauer af frie plus agglomererede ultrafine partikler i Danmark antages at være i intervallet 5-6 µg/m³ (sv.t. indholdet af forbrændingsrelaterede partikler)

Indeluft
På grund af de mange indendørs emissionskilder af ultrafine partikler anses niveauerne af (frie plus agglomererede) ultrafine partikler for at være højere end i udeluften.
Data vedrørende sundhedsrisici i forbindelse med indendørs partikelniveauer er imidlertid uhyre sparsomme, og på nuværende tidspunkt anvendes ofte de samme dosis-respons sammenhænge som for udeluftspartikler. Imidlertid bør det understreges, at der er store usikkerheder forbundet med denne fremgangsmåde, da den kemiske sammensætning af partiklerne kan være meget forskellig.

Nano-forbrugerprodukter
Der er endnu færre data til rådighed for risikovurdering af eksponeringen fra nanoprodukter end for vurdering af indeluftspartikler.
Selvom data om ultrafine partikler i luften vækker bekymring i forhold til eksponering fra forarbejdede nanomaterialer/nanopartikler, kan det på nuværende tidspunkt ikke anbefales at ekstrapolere risiko fra data for udeluftspartikler, da sammensætningen af partiklerne fra nano-forbrugerprodukter er helt forskellig fra sammensætningen af udeluftspartikler. En sådan

fremgangsmåde ville være baseret på gætteri frem for at være underbygget af videnskabelig argumentation.

Risikovurdering i relation til eksponering for nanomaterialer fra forbrugerprodukter må derfor for nærværende baseres på case-by-case vurderinger ved hjælp af data om de faktiske eksponeringsniveauer og faredata for de specifikke nanomaterialer. Selv om både eksponeringsdata og faredata i stor udstrækning savnes for mange nanomaterialer, begynder den øgede forskningsindsats inden for det seneste årti nu at fremkomme med nye oplysninger og en bedre forståelse af nanospecifikke egenskaber. Grundlaget for mere detaljerede risikovurderinger af nano-forbrugerprodukter er således voksende og vil øges yderligere i de kommende år.

1. Introduction

The aim of this work package of the project is to evaluate what risks consumers are exposed to from nanomaterials in the environment. The results should give proportionality to the possible risks from exposure to nanomaterials from use of consumer nano-products as described in other work packages of this project.

This report will summarise current knowledge on risk to Danish consumers from the environment including incidental nanomaterial exposure from particulate air pollution and exposure to nanomaterial generated when cooking food.

The work package shall:

- Survey reports and summarize the risk to consumers from incidental NM from traffic combustion and other sources of particulate air pollution
- Survey literature on current NM presence in drinking water and soil
- Asses the exposure to consumers from NM in drinking water and soil.

Further the findings regarding exposure to nanomaterials from the environmental media should be put into perspective to the exposure to nanomaterials from consumer products as assessed in another part of this project.

Humans have always been exposed to nanosized particles (also termed as ultrafine particles) from various natural sources, such as volcanism, fires, wood burning etc., however the number of anthropogenic sources have increased dramatically, during the last decade, mainly due to increased industrialization, diesel powered transport etc.. It has long been known that exposure to ultrafine particles could lead to adverse health effects in humans. For example ultrafine particles may in lung tissue lead to oxidative stress, mitochondrial damage and inflammation, and ultrafine particles seem to be more toxic compared to larger particles.

When considering the possible exposure to nanosized particles from the environment it is important to emphasize the differences between human made engineered nanomaterials and naturally occurring ultrafine particles.

The study of ultrafine particles is in connection with ambient air pollution a relatively old discipline compared to the study of engineered nanomaterials. Traditionally ultrafine particles have only been described in the matter of size and particle number concentration. The chemical composition is often not reported in studies on ultrafine particles.

So, while it on beforehand may be considered possible to some extent to evaluate nanoparticles from air, and compare this to exposure levels from nanomaterial in consumer products, it may be a greater challenge to find data on nanomaterials in soil and drinking water as exposures from these sources have not been in focus in relation the human health.

2. Ambient air

Ultrafine particles are non-engineered nanosized particles present in ambient air. There is a general consensus that ultrafine particles are defined as particles smaller than 100 nm in mobility diameter. Increased levels of these particles in urban settings mostly stem from combustion processes (WHO 2012; WHO 2013).

In the following sections the levels of nanoparticles/ ultrafine particles in ambient air and the sources for these particles is described. The overview will preferably relate to Danish measurements/data, however if data is lacking relevant international data will be used. The various sources for ultrafine particle emissions will be discussed and quantitative estimates regarding exposure to the Danish population will be given. Also it will be discussed to which extent data on hazards and risks are available on the ultrafine particles and to which extent it is possible to indicate risk estimates in relation to the exposures.

2.1 Measurement of nanoparticles/ ultrafine particles

Emitted primary ultrafine particles from e.g. vehicle exhaust are transformed rapidly due to coagulation, adsorption and secondary particle formation. However, also new particle formation from condensation or chemical reactions takes place in the air and may give rise to a high number concentration of particles in the nucleation and Aitken modes (0–20 nm and 20–100 nm) (WHO 2012).

Thus, ambient air particulates occur in different size modes, depending of the source of the particles and the age of the particles i.e. whether they have been freshly emitted or whether they had been subjected to physical or chemical alterations during aging.
Figure 2-1 below describes the various particle modes that are found in ambient air (Danish EPA 2008).

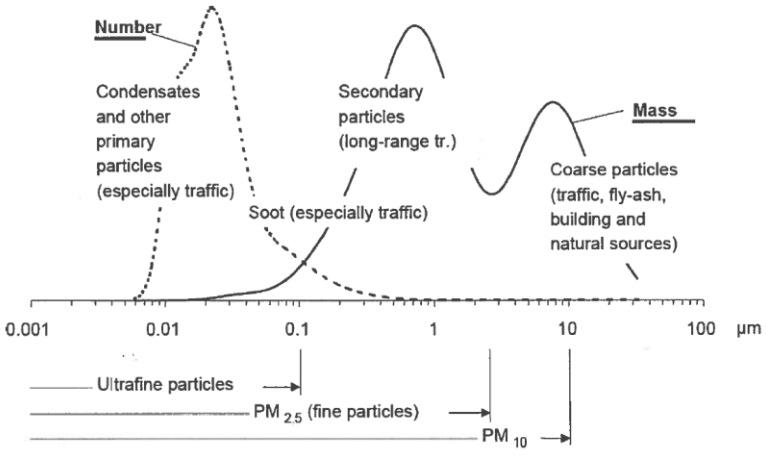


FIGURE 2-1. PARTICLE SIZE MODES IN AMBIENT AIR. NOTE THAT THE DOTTED LINE REPRESENTS PARTICLE NUMBER CONCENTRATIONS WHEREAS THE SOLID LINE REPRESENT THE MASS BASED CONCENTRATION (DANISH EPA 2008).

When measuring particulate matter (PM) this has traditionally been done by collection of the particulate matter on filters and by weighing the filters to obtain a mass based metric in *mg PM/m³* air. Depending of the pore size of the filter this is expressed as either *TSP* (total suspended particles); as *PM10* (particles below 10µm in diameter), or as *PM2.5* (particles below 2.5 µm). The particle size fraction PM2.5 is termed as fine particles, whereas the fraction PM10 minus PM2.5 is termed coarse particles (see Figure 2-1).
The content of soot in the air can be measured as black carbon (*BC*) by an optical method of the darkness of a white filter. BC measurement especially represent combustion related particles from e. g. diesel exhaust, residential wood or coal burning, power stations using heavy oil / coal or from vegetation fires. Another type of carbon measurement is elemental carbon (*EC*) which is measured by thermal-optical methods.
Today monitoring of air quality and limit values in relation to PM in ambient air is in relation to standard measurement of PM10 and PM2.5 and thus measurements stations all over Europe use stationary samplers for this purpose.
From epidemiological studies it has been shown that measurements of the PM2.5 level in general are best correlated to adverse health effects of ambient air particulates and this has put focus on the smaller size fractions of particulate matter including the g. ultrafine particles. These particles can also be measured on mass basis using special impactors or aerosol concentrators for obtaining enough ultrafine particles for mass based measurements (expressed as *PM0.1 in mg/m³*) or they may be measured on number basis (expressed as *particle number/cm³*) using optical measurement devices or particle counters.

The methodologies for measuring and characterization of ultrafine particles have developed fast, but currently no standards exist on the methods and no limit value or quality standard for ultrafine particles has been developed (either as mass *PM0.1* or as number i.e. *particle number/cm³*).

In principle there are two different types of spatial measurements: - *stationary measurements* giving information of the air quality and the particle concentration at a specific location (e.g. a street station in urban environment) or - *mobile, person borne measurements* where the measurement instrument is attached to the person and the instrument either collects particles for mass based personal exposure concentrations or makes particle counting and indicate particle number concentrations at different locations and during various activities of a person during a day.

As the ultrafine particles are very unstable in the air (due to rapid agglomeration into larger particles) high spatial variation pertains to the measurements of ultrafine particles. Thus exposure estimates for the population based on data from fixed measuring stations are much more subject to uncertainty and error for ultrafine particles compared to the exposure assessment for PM2.5 and PM10 where the levels are subject to less spatial variation (WHO 2012; WHO 2013).

2.2 Ultrafine particles in ambient air

2.2.1 Levels and composition/characterisation

2.2.1.1 Spatial and diurnal variation

The concentrations of ultrafine particles are highly variable spatially due to rapid agglomeration and therefore the levels of primary ultrafine particles decline rapidly with increasing distances from the roadways. Thus, the levels of ultrafine particles often differ substantially from one location to another within the same city. Due to their small contribution to mass (e.g. measured as PM2.5), ultrafine particles are not well reflected in PM mass measurements and they are not routinely monitored in most locations. Despite the high spatial variability of ultrafine particles, the number concentrations measured at various locations within cities tend to be reasonably correlated in time, rising and falling in similar patterns over the course of a day (HEI 2013).

The high diurnal variations in levels of ultrafine particles in urban air can be illustrate by the figure 2-2 below showing the fluctuations of the at a busy road in Copenhagen (HCAB), at urban background level in Copenhagen (HCOE) and at rural background level (LVBY) (NERI 2011).

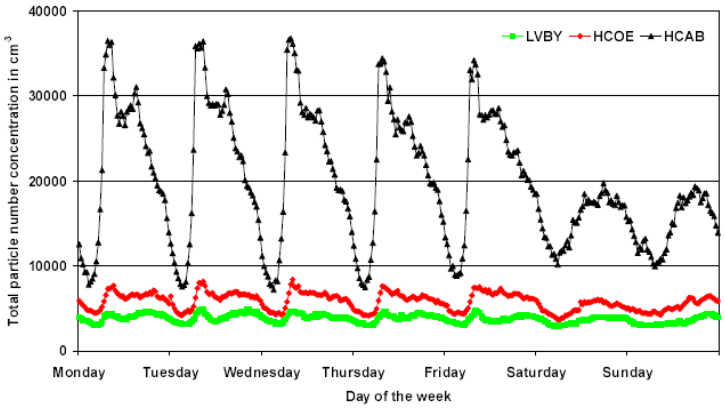


FIGURE 2-2 DIURNAL VARIATION OF TOTAL PARTICLE NUMBER CONCENTRATIONS OF ULTRAFINE PARTICLES. BLACK CURVE: BUSY STREET. RED CURVE: URBAN BACKGROUND. GREEN CURVE: RURAL BACKGROUND. (NERI 2011).

With respect to the ultrafine particle size distribution data from Danish EPA (2000) indicate that the highest number concentrations are obtained for particles having a diameter in the range of 10 to 50 nm (measured by Differential Mobility Analyser), see Figure 2-3.

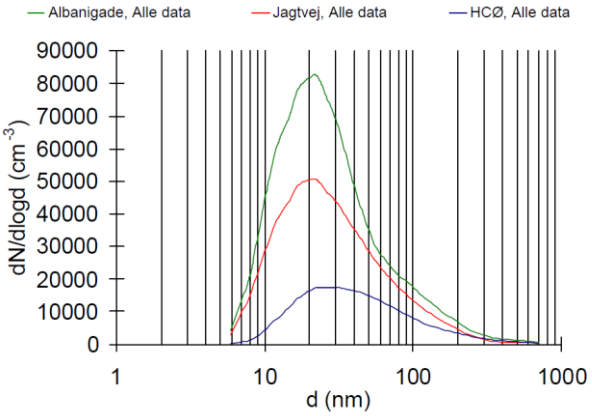


FIGURE 2-3 AVERAGE PARTICLE NUMBER CONCENTRATIONS AS FUNCTION OF PARTICLE SIZE. GREEN AND RED CURVES: BUSY STREETS; BLUE CURVE: URBAN BACKGROUND DANISH EPA 2000)

The highest number of concentrations were measured at busy streets in Albanigade in Odense (green curve) and Jagtvej in Copenhagen (red curve) compared to the urban background level in Copenhagen (blue curve). At Albanigade even short term peak concentrations exceeding 180 000 particles/ cm3 were measured.

The many factors influencing the particle number concentration and particles size distribution in air have been described in more detail Ketzel and Berkowicz (2004). The four factors: *dilution; coagulation (agglomeration); condensation and deposition* were found to be able to describe the fate of particles in air. The dilution process was found to be the dominating factor for a decrease in particle number concentration in the air. Dilution also affects the rate at which the other factors operate as these processes slow down when the air (or the exhaust) is diluted. Thus, coagulation is inversely proportional to the total particle number i.e. coagulation increase rapidly with increasing particle number (i.e. nearer to the source). Coagulation is very fast at removing the smallest

particle sizes and fastest for sizes of 8-20 nm. Condensation will not influence the total particle number concentration but will mainly remove particles below 15 nm as they by condensation of semi-volatiles grow to larger particles. A condensation rate (or particle growth rate) of 1-10 nm/hour was given for urban and rural locations. At the highest growth rate a 10 nm/hour condensation will dominate the removal of particles in the range of 15-20 nm with a factor 10 compared to removal by coagulation and deposition. Deposition especially plays a rule for particles above 50 nm where removal from deposition in general is faster compared to coagulation. All these factors may in a rather complex manner describe the dynamic processes that determine the particle numbers and particle sizes in the air at a given location. This also explains the reason for the very high spatial variability regarding particle number concentrations and particle size distributions within an urban environment where ultrafine particle numbers rapidly decline (and especially for the smallest particles) with increasing distance from the emission source.

2.2.1.2 Mean annual levels

In Denmark the following annual mean levels of ultrafine particles (measured as particle number concentrations) have been measured in ambient air (DCI 2012), Figure 2-4:

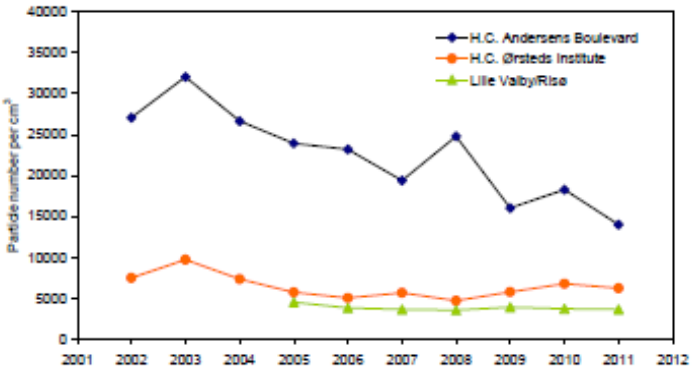


FIGURE 2-4 ANNUAL AVERAGES FOR PARTICLE NUMBER. BLUE CRUVE: BUSY STREET. ORANGE CURVE: URBAN BACKGROUND. GREEN CURVE: RURAL BACKGROUND. (DCE 2012).

The blue line represents particle levels at a very busy road in Copenhagen, whereas the orange line represents the background level of Copenhagen. The green line represents the rural background level. Thus the levels at a busy street contains additional *11 000-14 000 particles/cm³* compared to the rural background, whereas urban background contains additional approximately 2 000 particles per cm³ compared to urban background annual levels.

In 2011 the average level of PM2.5 in Copenhagen (at the busy road) was about 20 µg/m³ and the average number concentration was about *15 000 particles /cm³*, whereas, in rural background the figures were about 15 µg/m³ and *4 000 particles/cm³*.

As indicated in Figure 2-5 the vast majority of these particles are within the lower nano size range (The measurements have been carried out using a Differential mobility particle sizer (DMPS) that counts particle with mobility diameter between 6 and 700 nm).

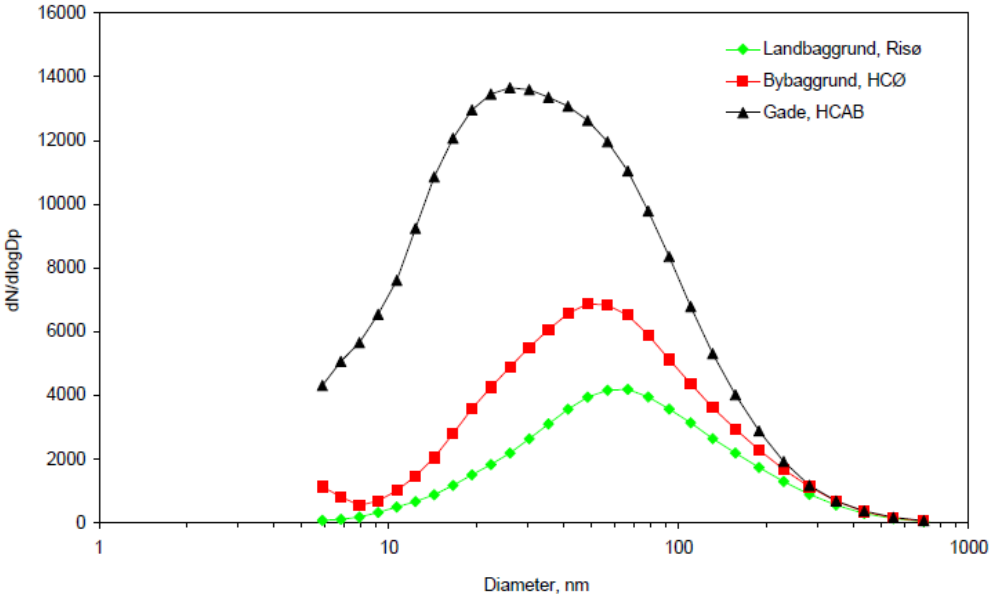


FIGURE 2-5. AVERAGE PARTICLE SIZE DISTRIBUTION MEASURED IN 2011. BLACK CURVE: BUSY STREET. RED CURVE: URBAN BACKGROUND. GREEN CURVE: RURAL BACKGROUND. (DCE 2014)

Differences pertain to the particle size modes at busy streets and at urban background or rural background. Figure 2-5 shows the annual average of particle number measurements at a busy street and at urban and rural backgrounds. The figure further indicates that highest levels for ultrafine particles are reached at a particle diameter 20-30 nm for busy streets whereas the particle number peak at higher particle sizes for urban and rural background (DCE 2014).

2.2.1.3 Composition

The composition of the ultrafine particles from combustion is mainly elemental carbon, soot and organic carbon. Organic carbon particles may be generated as *secondary organic aerosols* which are particles generated from gases of volatile organic carbons (biogenic or anthropogenic) that have reacted with atmospheric oxidants such as O3, NO3 or OH to form low-volatility products (particles) (NERI 2011).

The Table 2- 1 below shows the daily average urban and country site levels of elemental carbon, EC and organic carbon, OC in Denmark in 2011.

TABLE 2-1. AVERAGE LEVELS OF ELEMENTAL CARBON (EC) AND ORGANIC CARBON (OC) AT A BUSY STREET IN COPENHAGEN AND AT RURAL BACKGROUND IN LILLE VALBY (DCE 2012)

Concentration µg/m^3	Number of results	EC, average	90% percentile
Copenhagen/ 1103	342	2.43	3.63
Lille Valby/ 2090	353	0.38	0.88

Concentration µg/m^3	Number of results	OC, average	90% percentile
Copenhagen/ 1103	342	2.56	4.60
Lille Valby/ 2090	353	1.53	2.96

EC and OC were determined by thermal/optical analysis of the filter samples.
Polyaromatic hydrocarbons (PAH) are a part of organic carbon and are especially considered of concern with respect to ultrafine particles and ambient air pollution. In Copenhagen the sum of the five PAH substances listed as relevant in the EU Ambient Air Directive was in 2011 measured to be below 10 ng/m^3 even in the winter months, and the level of benzo(a)pyrene was below 0.5 ng/m^3 (DCE 2012)

The levels of organic carbon and elemental carbon (that to a great extent contain ultrafine particles) may be compared to the levels of fine particles PM2.5 in ambient air from urban and rural areas, Figure 2-6.

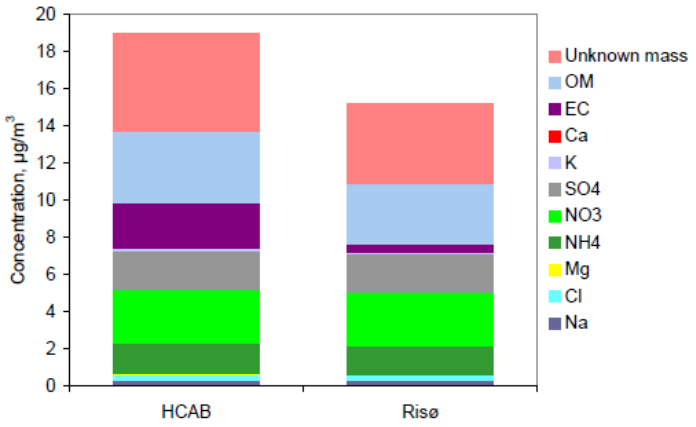


FIGURE 2-6 ANNUAL AVERAGE CONTRIBUTIONS TO THE CHEMICAL COMPOSITION OF PM2.5 AT A BUSY STREET IN COPENHAGEN (HCAB) AND AT RURAL BACKGROUND IN RISØ (DCE 2012).

From this it can be seen that organic matter (OM) together with elemental carbon (EC) make up about ¼ - 1/3 of the PM2.5 levels. It has been shown that PM2.5 levels with high contents of combustion related OM and EC (i.e. a high contribution from ultrafine particles) are especially related to adverse effects to human health.

Weight of ultrafine particles
Gugamsetty et al. (2012) made eighteen 24 hours measurements during the cause of 6 months in an urban area in Taiwan and found that OM and EC contributed with 26.6% and 5.4% of the average PM2.5 level of 21.8 mg/m^3. The PM0.1 level was found to contribute with 1.4 mg/m^3, i.e. 6.4% of the PM2.5 level. The PM0.1 fraction was dominated by vehicle emission 25%; secondary aerosols 37% and industrial emissions 16% with soil dust and salt only contributing with 13%.

Geller et al. (2002) measured the levels of ultrafine particles at a "source" site impacted by fresh heavy truck diesel emissions and a "receptor" site representing secondary photochemical reactions particles and urban background levels. The average levels from three measurements over the day were 2.5 x 10^4 particles/cm^3 with an average mass of 1.20 µg/m^3 for the "source" site, and 1 x 10^4 particles /cm^3 with an average mass of 0.74 µg/m^3. These data also indicate a rather low mass based contribution from the ultrafine particles.

2.2.1.4 Overall

The fraction of ultrafine particles in ambient air is mainly due to combustion related sources and the levels of these may either be reflected in measurements of particle number (measurement of free ultrafine particles) or in mass based metrics such as black smoke, soot, elemental carbon or organic carbon which is dominated by ultrafine particles (either as free or agglomerates particles). In general these fractions make up 25-33% of the PM2.5 content in ambient air for background levels and for urban street stations.

2.2.2 Sources

The formation of nanometer sized atmospheric aerosol particles has been observed to occur at all geographical sites in the world. Sulphuric acid is considered one of the key elements contributing to the initial step of the formation if new atmospheric particles. Typical formation rates of 3 nm particles varied from 0.01 to 10 particles/cm^3 /second. One order of magnitude higher formation rates were detected in urban environment. Highest formation rates up to 10^5 particles/cm^3/second were detected in coastal areas and in industrial pollution plumes. Subsequent growth rates varied from 0.01 to 20 nm/hour. The largest growth rates were observed in the polluted urban environment.

In Table 2-2 below overall estimates for point source appointment for PM10 and PM2.5 for a rural background area in Denmark were given. The estimates are based on sampling in during a campaign in 2008-2009 and following chemical analysis of the samples (NERI 2011).

TABLE 2-2 SOURCE APPOINTMENT OF PM2.5 AND PM10 LEVELS IN A RURAL BACKGROUND AREA (LILLE VALBY) IN DENMARK BASED ON MODELLING AND CHEMICAL ANALYSIS. MASS GAPS SHOW THE DIFFERENCE BETWEEN MODELLED AND MEASURED PM CONCENTRATIONS (NERI 2011)

	PM_{10} (µg/m^3)		$PM_{2.5}$ (µg/m^3)		$PM_{2.5}/PM_{10}$
PM modelled	13.78		8.91		58%
PM measured	16.65		13.15		78%
Salt	1.42	15%	0.09	2%	12%
$NaNO_3$	1.07		0.22		
NH_4NO_3	2.88	28%	2.20	28%	80%
$(NH_4)_2SO_4$	1.28		1.20		
$(NH_4)HSO_4$	0.60		0.40		
Rock	0.34	2%	0.02	0.2%	6%
Lime	0.16	1%	0.01	0.1%	8%
Biomass	1.87	11%	1.27	10%	68%
Oil	1.15	7%	0.64	5%	56%
Coal	0.81	5%	0.68	5%	84%
Vehicle	0.29	2%	0.09	0.7%	31%
SOA*	1.92	11%	2.10	16%	109%

	PM_{10} (µg/m³)		$PM_{2.5}$ (µg/m³)		$PM_{2.5}/PM_{10}$
Mass gap	3.28	19%	4.43	33%	165%

From the data on PM2.5 it can be seen that biomass, oil, coal, vehicle, *SOA (secondary organic aerosols) which are considered significant sources for ultrafine particles make up 37% of the total PM2.5 or 4.9 µg/m³.

NERI (2011) indicates the following sources that especially are considered responsible for levels of ultrafine particles in ambient air:

- Biofuel combustion (domestic wood burning, forest fires etc.)
- Oil combustion
- Coal combustion
- Vehicles
- Secondary organic particles generated from oxidation of VOCs and semi-VOCs

For the other sources of *inorganic salts* and *mineral particulates* it is very uncertain how much they contribute to the levels of ultrafine particles in the air.

No specific estimations have been made regarding the various emission sources and their relative contribution to the emission of ultrafine particles in Denmark. For the annual Danish emissions of PM2.5 in 2005, however, the contribution from the following sources has been assessed to:

Traffic exhaust: 13% of PM2.5 emissions (about 3500 tonnes PM2.5)
Domestic wood burning: 64% of PM2.5 emissions (about 17 000 tones PM2.5)
Other combustion: 14% of PM2.5 emissions (about 3700 tonnes PM2.5)
(DMU 2009)

It may be anticipated that a very large fractions of these combustion related sources are emitted as ultrafine particles, that then after short time in air agglomerates to larger particles.

On a European scale a total emission of 271 000 tonnes of *ultrafine particles (PM0.1)* into ambient air has been estimated for EU27 for year 2008 (Amec 2011). The following sources dominated this emission:

Road transport:	93 000 tonnes	(34%)
Non-road transport:	59 000 tonnes	(22%)
Residential and commercial (combustion):	41 000 tonnes	(15%)
Industrial combustion +power generation:	43 000 tonnes	(16%)
Agriculture:	22 000 tonnes	(8%)
Industrial processes:	12 000 tonnes	(5%)

This overall annual tonnage level of 271 000 tonnes of ultrafine particles contributed with 13% to an overall estimated annual emission of 2 092 000 tonnes PM10. For road transport, however, the ultrafine fraction contributed with 32% of the PM10 particle emission.

The possible contribution of manufactured nanomaterials have not been included in these emission figures as the contributions from manufactured nanomaterials were not possible to trace due to lack of emission data.

2.2.2.1 Traffic

The particle contribution from traffic has been studied in details in Copenhagen, recently by the National Environmental Research Institute (DCE 2012). The particulate matter in Copenhagen

shows a diurnal variation that follows the traffic pattern. This confirms the finding that particles to a great extend are generated locally by traffic.

Exhaust from diesel engines includes three basic components: elemental carbon particles; organic matter adsorbed onto the surface of the carbon particles; and a mixture of gas and vapour phases that include volatile organic compounds (WHO/IARC 2013). Thus, the composition of the ultrafine particles from combustion such as traffic is mainly elemental carbon, soot and organic carbon.

Organic carbon particles are generated as *secondary organic aerosols* that are particles generated as condensation products from gases of volatile organic carbons or from the reactions with oxidants in the air. At busy roads these fractions may contribute to up to 1/3 of the PM2.5 levels or around 6-7 μg/m^3 (HCB in Copenhagen, see figure 3-5). In rural background these fractions made up about 4 μg/m^3 indicating further contributions in busy road from the local traffic (DCE 2012).

In urban area (Copenhagen) *traffic* (vehicles) is considered to be the dominant source to the soot particles in ambient air. The exhaust from road traffic at a busy road was estimated to contribute with 4 μg/m^3 PM2.5 in the ambient air. Contributions from *trains* were further measured to 0.05 – 0.9 μg/m^3 PM2.5, depending of the distance from the railway (NERI 2011, Danish EPA 2013). Although not measured as ultrafine particles these fractions of the PM2.5 may to a great extent (or mostly) contain ultrafine particles plus agglomerates hereof.

Measurements of size distribution of urban particle matter show that the average diameter increases from the street level to urban background and rural background. The annual average total particle number (range 6-700 nm), was around 16 000 particles per cm^3, at a road with heavy traffic. As a comparison the rural background was measured to be 3 800 particles per cm^3.
A decrease in the levels of the smallest particles (6-40 nm), was observed over the period 2002-2010. This can be attributed to improvements of the vehicle fleet, such as newer cars and particle filters but may also partly be attributed to new asphalt surface leading to reduced generation of particles by road abrasion (DCI 2012).

It is well-known that nanoscale cerium oxide (CeO2) is used as a fuel additive in diesel for increasing fuel combustion efficiency and decrease diesel soot emissions. Despite efficient trapping of particulate matter (soot), engine tests have shown small amounts of CeO2 in diesel exhaust. Thus, studies in the UK (London and Newcastle) have shown typical levels of 200-700 pg Ce/m^3 (i.e. 0.2-0.7 x 10^{-3} μg Ce/m^3) (Casse et al. 2011).

2.2.2.2 Wood smoke

Wood smoke is another important factor for fine and ultrafine particles in ambient air. It has been estimated that about 64% (or about 1665 tonnes PM2.5) of the total PM2.5 *emissions* in Denmark in 2005 could be attributed to wood burning from about 551 000 wood stoves and 48 000 wood boilers in Denmark (Danish EPA 2008).

Measurements during a 6-week winter period (2002 and 2003-2004) in a Danish residential area with no district heating and many wood stoves showed that the contribution from wood combustion to ambient PM2.5 was comparable to the contribution from a heavily trafficked road to PM2.5 at the sidewalk. The average local PM2.5 contribution ion ambient air from wood combustion was about 4 μg/m^3. In another residential area with natural gas combustion as the primary heating source and wood combustion as a secondary heating source, the average PM2.5 concentration was elevated by about 1 μg/m^3 compared to background measurements during four winter weeks. An increase in annual average PM2.5 of 1 μg/m^3 is a best maximum estimate for the whole Danish population exposure based on the data from the measurements in these two residential areas (Danish EPA 2008).

Based on the *total particle emissions* from residential wood burning, model calculations have been used to estimate the contribution to the annual PM2.5 levels. The results showed an increase in annual PM2.5 of 0.2 µg/m^3 (as a best minimum estimate) as an average for the whole Danish population. In conclusion, the annual average PM2.5 exposure from wood smoke was roughly estimated to be 0.2-1 µg/m^3 for the whole Danish population with a best estimate of about 0.6 µg/m^3 (Danish EPA 2008).

2.2.2.3 Waste incineration and energy production

For Denmark it has been estimated that energy plants have a total annual PM2.5 emission of 354 tonnes of which incineration plants contribute with 26 tonnes. This corresponds to 1.3% and 0.14% of the total annual Danish PM2.5 emissions, respectively (DMU 2009).

When waste is incinerated, for example in waste to energy (WTE) plants, considerable amounts of ultrafine particles are being released into the ambient environment. Cernuschi et al. (2012) studied the concentration and chemical composition of ultrafine particles released from WTE plants in Italy. Average ambient levels measured at stack release for the size range 0-100 nm, were in the range of 5 x 10^3 to 6 x 10^5 particles/cm^3 for various sample conditions. Ionic compounds, chlorides, nitrates and ammonium accounted for roughly 46% of the total particulate mass, and trace metals accounted for 22% of the mass, mainly chromium, iron, nickel, zinc and lead.

Buonanno et al. (2011) investigated the release of ultrafine particles emitted from a WTE plant. They found that ultrafine particles release after filtration, mainly consisted of various metal oxides, inorganic salts and silicates. In addition they found that metals with melting point below 1200°C (arsenic, cadmium and zinc) decrease in contribution to particle mass, with increase particle size and metals with higher melting point than 1200°C increase in contribution to particle mass with increasing particle size. The reason for this might be that the metals with high melting point will remain in the solid phase and act as nuclei and leading to larger diameters via condensation phenomena. Maximum particles released after the filter from the WTE plant was 2.0 x 10^3 particles/cm^3, with an average of 1 x 10^3 particles/cm^3.

2.2.2.4 Natural sources

Amec (2011) estimated the non-anthropogenic emissions of ultrafine particles to account for 7000 tonnes in EU27 (i.e. 2.6% of the anthropogenic emissions of ultrafine particles). About 50% of this emission was anticipated to derive from biomass burning (e.g. forest fires) and about 50% from volcanoes.
It should be noted that these estimates were based on several assumptions (especially the estimate for volcano ash) and therefore subject to large uncertainties.

The oxidation of organic volatile compounds (VOCs) from both biogenic (as well as from anthropogenic origin) is able to produce new particles in the atmosphere.
The contribution from forests have been measured by Chen et al. (2010) that found high diurnal variations of the content of ultrafine particles in a forest in Taiwan. Peak levels were found in the afternoon reaching a level of 12 000 particles/ cm^3 and levels down to 1000 particles/cm^3 were found during the night.

Ultrafine particles have also been measured in relation to the generation of sea salt particles. Pierce (2008) reported levels of 400-1500 particles /cm^3 with the highest levels of the southern hemisphere. At the northern hemisphere at altitudes comparable to the location of the Denmark levels of about 500 particles /cm^3 and a size mode of 20 nm.
These hygroscopic particles grow to larger sizes and occur mainly as larger particles in the PM2.5 and PM10 measurements.
Amec (2011) referred to an observation in a remote marine area where 60% of the content of ultrafine particles in air were due to sea salt (-as particle number or by weight was not indicated).

Overall, however, ultrafine particles from sea salt was not considered to be a significant source of the mass (PM0.1) of ultrafine particles in air.

Also, Amec (2011) considered the contribution from windblown dust to be negligible in terms of contribution to the PM0.1 levels in ambient air.

2.2.2.5 Overall

The dominant sources for ultrafine particles in ambient air in Denmark are combustion related sources. Of these domestic wood burning and traffic exhaust were representing 64 and 13% of the annual PM2.5 emission in Denmark in 2009, whereas other combustion sources represented 14%. It may be anticipated that a very large fraction of these combustion related sources is emitted as ultrafine particles, that then after short time in air agglomerates to larger particles.
It is not possible based on the available data to give any indication of the fraction of ultrafine particles that stems from natural sources such as e.g. ultrafine particles generated from sea salt or from ozone reactions with VOCs emitted from forests.

2.3 Exposure

Exposure

The concentration levels above are in relation to stationary measurements. These measurements may be used as rough proxy for outdoor exposure to the population living in the area. Exposure assessment for the population may, however, be further refined when obtaining data of the address of the individual persons in the population, their activity pattern, their distance to the measurements stations and the meteorological conditions.

Another way to gain more insight into individual exposure of a person is by characterising and measuring exposure by using portable measuring devices.

Vinzents and co-workers in 2005 reported the concentration of ultrafine particles in the breathing zone in 15 young and healthy volunteers in Copenhagen using portable instruments for measuring particle number concentrations. The average exposure level during biking in traffic was 32.4 x 10^3 particles/ cm^3 whereas average exposure was 19.6 x 10^3 particles/ cm^3 at other outdoor locations. The average indoor level was measured to 13.4 x 10^3 particles/ cm^3. The reporting of the time activity pattern indicated that the far highest exposure to ultrafine particles was attributed to indoor exposure as 100 minutes covered time spent outdoor biking, 62 minutes other outdoor activities and 751 minutes indoor activities (Danish EPA 2005).

Figure 3-7 below indicates the considerable variation in exposure for a person to ultrafine particles during a day. As can be seen the far highest peak exposure was obtained indoors during cooking. Also, it can be seen that exposure in traffic out-doors is made up by many peak exposures rather than a constant exposure level.

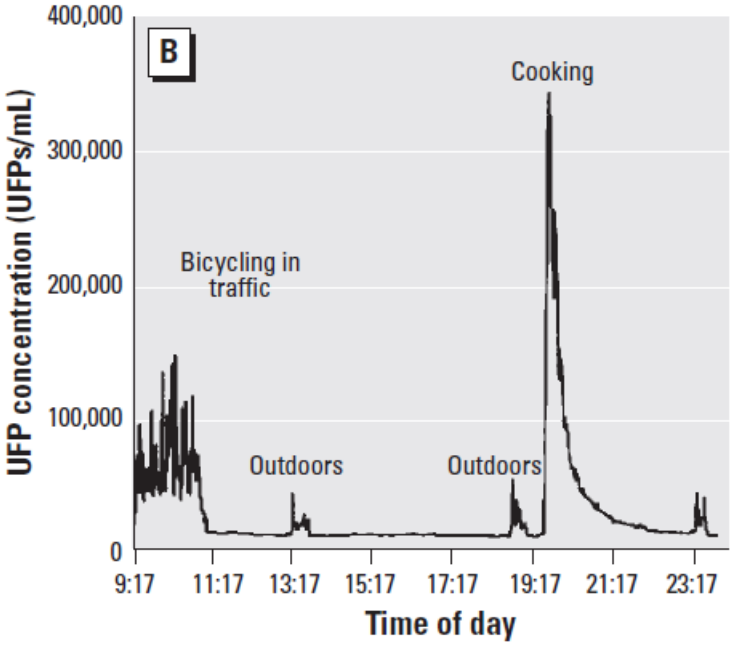


FIGURE 3-7 TIME SERIES MEASUREMENT OF ULTRAFINE PARTICLES ON A TEST DAY WHEN BIKING IN TRAFFIC DURING RUSH HOUR IN COPENHAGEN (DANISH EPA 2005; VINZENTS ET AL., 2005))

Using 30 volunteers Sørensen et al. (2005) measured personal exposure as well as bedroom, front door and background concentrations of PM2.5, black smoke (BS) and nitrogen dioxide (NO2) during two-day periods in Copenhagen during winter, spring summer and autumn.
The following data, Table 2-3 was obtained for the PM2.5 measurements:

TABLE 2-3 PERSONAL PM2.5 EXPOSURE LEVELS (SØRENSEN ET AL. 2005)

	PM2.5 (µg/m³)			
	Median	Q25-Q75	Median	Q25-Q75
Personal	17.5	13.1-27.7	11.9	8.5-23.1
Home indoor, bedroom	13.4	9.4-20.6	9.5	6.5-15.5
Home front door	9.2	6.1-13.7	7.8	4.4-13.0
Urban Street station	16.5	12.4-23-3	12.4	8.8-15.5
Urban background	10.2	7.4-14.8	6.6	5.0-12.9

For PM2.5 the bedroom and the front door concentrations were found to be significant predictors of the personal exposure, whereas background levels reached borderline significance. For BS a similar pattern was seen with the exception that background concentration was far from being a significant predictor. (This indicates that estimation of front door exposure as done in several epidemiological studies is a better proxy for the personal exposure as the background exposure). The bedroom concentrations were the strongest predictor for the personal exposure for all the three pollution measurements. The association between front door and background concentrations was significant for PM2.5 and NO2.

For PM2.5 a 2.3% increase and a 7.8% increase of personal exposure was estimated per 1% in time exposed to environmental to tobacco smoke or candle light burning, respectively. For black smoke a 10.5% increase (absorbance measurements) was found for 1% increase in time of candle burning. Further it was found that personal PM2.5 exposure was more affected to indoor sources than BS and NO2, indicating BS and NO2 to be more strongly associated to traffic than PM2.5. Ambient background BS level was found to be an unsuitable predictor for personal exposure. Furthermore the data indicated that BS and NO2 more strongly penetrate into building compared to PM2.5.

Quiros et al. (2013) measured particle number concentration at an urban street in Santa Monica in California and the personal exposure during different four transport conditions (the same trip by walking, cycling, driving in a car with either closed or open window). The median level of ultrafine particles was measured to 1-3 x 10^4 particles/cm^3. Respiratory ultrafine particle exposure (i.e. particles inhaled per trip) was compared to driving with closed windows: ≈2 times higher when driving with open car window; ≈15 times higher when cycling, and ≈30 times higher when walking.

Berghmans et al. (2009) measured the levels of ultrafine particles in connection with cycling during seven mornings in the rush hours in a town in Flanders, Belgium. The number concentration was as an overall average measured to 21.2 x 10^3 particles/ cm^3. Mass based particle levels were measured as well as either PM1, PM2,5 PM10 and TSP, however, *no correlations* between ultrafine particle levels and either of the mass based metrics could be found.

Fruin et al. (2008) estimated daily exposure to ultrafine particles by typical activities in a common micro-environments in Los Angeles. Although only spending a total of 1 hour in a car on freeways (90 000 -240 000 particles/cm^3 in-site car) and on arterial roads (33 000-58 000 particles/cm^3 in-site car), the exposure to ultrafine particles from this accounted for 36% of the total particle number exposure during a day (24 hours with a time weighted average of 14 000 particles/cm^3). One hour outdoors at an average concentration of 21 000 particles/cm3 accounted for 6% of the daily exposure.

2.4 Health effects of particles and ultrafine particles in ambient air

This section covers a description of the adverse health effects of particulate matter (including ultrafine particles in ambient air). Knowledge regarding specific and independent effects from ultrafine particles compared to i.e. PM2.5 is still lacking, however the role of ultrafine particles and its constituents in relation to the adverse effects is currently intensively discussed.

According to WHO (2006) and WHO (2013) series of adverse effects on health of particulate matter are well documented by epidemiological studies and from experimental animal studies. Overall, it was found that there is no evidence of a safe level of exposure to ambient air particles or a threshold below which no adverse health effects occur. Thus the particles in ambient air are concluded to create a substantial burden of disease, not at least by reducing the life expectancy by almost 9 months on average in Europe.

2.4.1 Hazards

WHO (2006) summarized adverse effects from acute and *long-term* exposure to particulate matter as follows based on the human evidence from epidemiological and clinical studies:

- mortality and hospital admission in chronic obstructive pulmonary disease (COPD) patients
- exacerbation of symptoms and increased use of therapy in asthma
- mortality and hospital admission in cardiovascular disease patients
- mortality and hospital admission in diabetes mellitus
- increased risk for myocardial infarction
- lung inflammation

• systemic inflammation
• endothelial and vascular dysfunction
• development of atherosclerosis
• increased incidence of infection
• respiratory cancer

The following dose-responses were presented for daily mortality in relation to *short term* exposure studies (in relation to changes in 24-hours PM2.5 levels) and mortality in relation to *long-term* exposure studies (in relation to average annual PM2.5 levels)

TABLE 2-4 RISK ESTIMATES FOR PM EXPOSURE (WHO 2006)

Outcome	Source	Reference	Estimate	95% CI
Daily mortality (all-cause)	WHO meta-analysis	WHO (2)	0.6%/10 µg/m^3	0.4-0.8
Daily mortality (respiratory)	WHO meta-analysis	WHO (2)	1.3%/10 µg/m^3	0.5-2.09
Daily mortality (cardiovascular)	WHO meta-analysis	WHO (2)	0.9%/10 µg/m^3	0.5-1.3
Daily mortality (all-cause)	NMMAPS revised	Health Effects Institure (243)	0.21%/10 µg/m^3	0.09-0.33
Daily mortality (cardiovascular)	NMMAPS revised	Health Effects Institure (243)	0.31%/10 µg/m^3	0.13-0.49
Long-term mortality (all-cause)	ACS CPS II 1979-1983	Pope et al. (323)	4%/10 µg/m^3	1-8
Long-term mortality (cardiopulmonary)	ACS CPS II 1979-1983	Pope et al. (323)	6%/10 µg/m^3	2-10

Comment:
As can be seen from Table 2.4 the increase in mortality from long-term exposure studies is much higher (4—6% increase in mortality per 10 µg/m^3 of PM2.5) than in relation to short term exposure studies on daily mortality (0.21 - 1.3% increase in mortality per 10 µg/m^3 of PM2.5). This indicates that adding the effects from all short term peaks will grossly underestimate the mortality from long-term exposure and that that average background exposure level underneath the peak exposures is the dominant cause to the increased mortality. Thus, mortality associated to peak exposures may be seen as harvesting effects that may forward the fatal episodes in time.

2.4.2 Mechanistic considerations

According to WHO (2006) it was not possible to conclude whether the biological effects were due to the particle's presence rather than to its specific chemistry and to which extent the effects were also particle-size-dependent.
Evaluation of size as a modulating factor in PM toxicity was considered very difficult since size is not independent of chemical composition, i.e. certain size modes tend to contain certain chemical components, such as metals in the fine mode and crustal materials in the coarse mode. Also, there are clear differences between particles in different size modes in terms of deposition and retention rates within the respiratory tract.

However, WHO (2006) suggested that for ultrafine particles, size itself rather than chemical composition may determine toxicity as e.g. ultrafine particles appeared to produce a more

significant pulmonary inflammatory response than that produced by fine particles having the same chemical composition and at the same exposure mass concentration . However, since for a given mass concentration an atmosphere consisting of ultrafine particles will have a greater number concentration than one consisting of fine particles, as well as a greater total surface area available for adsorption of toxic chemicals, exposure dose would actually be greater for ultrafine than for fine particles compared with these other exposure metrics.

A potential mechanism for enhanced effects of ultrafine particles was considered to be more effective translocation from the respiratory tract to extra-pulmonary sites in the body compared to larger particles. For example, ultrafine elemental carbon particles inhaled by rats were found in brain tissue, and have been suggested to reach the brain via translocation along the olfactory nerve following deposition on the olfactory mucosa of the nasal region. In this way the protective blood–brain barrier of the central nervous system is circumvented, and provides a direct route for inhaled PM into the nervous system without transport via the systemic circulation. Furthermore, ultrafine particles have also been found to translocate from the respiratory tract to the liver.

The ability of PM to elicit inflammatory cytokine production and to cause lipid peroxidation was found to depend on particle size, being most evident for the ultrafine particles. The relationship between response and specific chemical components was less definite, suggesting that the observed responses were associated either with different sets of particle components within each size mode or with nonspecific size effects.

However, looking across the currently available toxicological evidence, there is little indication that any single physical or chemical property of PM is responsible for the array of adverse health outcomes reported in epidemiological studies. Toxicological studies do, however, indicate that primary PM generated from fossil fuel combustion processes, notably vehicular emissions, may be a significant contributor to adverse health outcomes. These emissions generally have a high content of organic carbon and some metals, and may have large PM surface area and number concentration. Regardless of these promising leads, the evidence cannot yet (i.e. 2005) support an indicator for a standard that is more specific than size fractionated mass alone (WHO 2006).

WHO (2013) in an updated review assessing the data published since the WHO (2006) evaluation found that additional scientific data supported and strengthened the conclusions made by WHO (2006). In addition the further adverse health end-points were found to be linked to PM:

- adverse birth outcomes
- neurodevelopment and cognitive function

WHO (2013) also made a review on the evidence on the various fractions in particulate air pollution including ultrafine particles and combustion related constituents e.g. ultrafine particles and elemental carbon and organic carbon. It was concluded that the evidence for the harmful effects of traffic generated particles has become even stronger even though it is still not possible to appoint a specific estimate on the relative contribution to the harmful effects in quantitative terms. Also new studies suggested that cardiovascular mortality in relation to particle exposure from biomass combustion may be comparable to the effects from traffic-related particles.

WHO (2012a) looking at health effects of black carbon as well as WHO (2013) referred to a study by Janssen et al. (2011) that examined to which extent the adverse health effects from PM2.5 could be ascribed to combustion related black carbon particles (BCP) (measured as either black smoke (BS), black carbon (BC), elemental carbon (EC) or absorbance (Abs)). From review of the literature it was found that a relatively large part 40-70% of the roadside PM2.5 increment above background level is to be attributed to BCP.

For making comparison EC was used as a measure for BCP, and a relation of 10 μg/m^3 BS = 1.1 μg/m^3 EC was used . This relationship was found from the average from 11 studies including both measures.
When studying acute effects from time-series studies the effects (daily mortality or number of hospital admissions) per 1 μg/m^3 (averaged over 24-hours) were generally one order of magnitude higher for the BCP measure compared to the PM2.5 measure. However the magnitude of the effects analysed on the basis of interquartile differences of the pollutants levels were rather similar for PM2.5 and BCP. When using statistical two-pollutant models on the data from these studies it was found that the effect of BCP was more robust than the effects of the PM metric.
From a analysis 4 long-term mortality studies it was found that per 1 μg/m^3 (as annual average) the effects of EC was 5-14 times higher for all-cause mortality than for the PM2.5 metric.
Based on these results it was concluded that BCP should be considered as a valuable indicator of the health risks of air quality dominated by primary combustion particles.

WHO/IARC (2013) has evaluated the evidence for the carcinogenicity of diesel and gasoline engine exhaust. From the review of the epidemiological and experimental animal data it was concluded that there is sufficient evidence in humans for the carcinogenicity in the lungs of diesel engine exhaust. A positive association was further observed between exposure to diesel engine exhaust and cancer of the urinary bladder.
In experimental animals there was sufficient evidence for the carcinogenicity of whole diesel engine exhaust and diesel engine exhaust particulate matter together with sufficient evidence in relation of exposure to extracts of diesel engine exhaust particles.
For gasoline engine exhaust there was only found sufficient evidence for the carcinogenicity of condensates from the gasoline exhausts in experimental animals

The *Health Effects Institute* in the US recently made a survey specifically regarding the health effects of *ambient ultrafine particles* (HEI 2013). Having surveyed both the experimental human and experimental data as well as the epidemiological data the following findings were summarised:

From the experimental data it was found that ultrafine particles:
- have a greater potential than fine particles to be retained in the lung
- may enter the blood stream and move beyond the lung
- may enhance allergic responses
- may translocate to the brain from the nose
- may cause respiratory and cardio/vascular effects

Further, it was observed in relation to the epidemiological data:
- lack of consistent data for ultrafine particle and associations to respiratory and cardiovascular effects
- failure to show any independent effects of ultrafine particles compared to other PM metrics

Also, it was emphasised that experimental animal *long-term* testing is lacking and that the human clinical findings (mostly short-term exposure) are considered inconsistent.

Thus it was considered difficult by (HEI 2013) to draw more firm conclusions based on the existing database on ultrafine particles.

2.4.3 Most relevant metric in relation to adverse health effects

Overall, the strongest and most robust associations regarding adverse health effects and particles levels in air have been found in relation to PM2.5 measurements. Thus the levels of PM2.5 may be seen as a good indicator for the exposure of the population as well as the adverse health outcome.
Regarding dose-response relationship higher potency of the PM2.5 levels have been found with increased relative content of combustion related constituents. As these combustion related

constituents, such as soot, elemental carbon and organic carbon, mainly are derived from agglomeration of ultrafine particles this provides a strong indication that the fraction of agglomerated ultrafine particles are having a crucial role in relation to the health effects of particle matter.
The association between exposure to free ultrafine particles in air (measured as PM0.1 or particle number concentration) and adverse health outcome is far less consistent. This may very well be due to the fact that the amount of ultrafine particle in free phase in the air is much lower than the amount of agglomerated ultrafine particles. In addition to this the levels and the exposure to free ultrafine particles is subject to very high spatial variations and thus it may be difficult to use single or few measurements of PM0.1 or particle number concentrations as a good indicators for the population exposure. This of course makes it very difficult to find robust associations between free ultrafine particles in air and adverse health outcomes.
Therefor when assessing the effects of the sum of ultrafine particles (free and agglomerated particles) PM2.5 measurements especially in areas dominated by combustion related sources may be a good indicator for the adverse health effects of ultrafine particles (and a far better indicator as measurements of the free fraction of ultrafine particles measured as particle numbers or PM0.1). Another good measurement of soot nanoparticles is the content of elemental carbon in the air (or BC).

2.4.4 Recent data on effects from ambient air pollution in Denmark

Andersen et al (2010) recently studied the possible association between short-term exposure to ultrafine particles in the Copenhagen area and hospital admission for stroke. A mean 24-hours level of 6 365 ultrafine particles/cm^3 particles was estimated with an interquartile range of 4 033-7 951 particles/cm^3 based on street and roof measurements and mean PM10 levels of 27.1 µg/m^3 with an interquartile range of 9.8 - 18.6 µg/m^3 was based on monitoring data for the period 2003-2006. A 21% increased rate of hospitalizations for mild ischaemic stokes was found in connection with an increase of 3 918 particle/cm^3 (the interquartile range of the exposure), i.e. and increase of 5.4% for an increase of 1 000 particles/cm^3.

Raaschou-Nielsen et al (2011a) found a strong significant association between long-term exposure to traffic-related air pollution and the occurrence of lung cancer. The cohort consisted of nearly 53 000 persons from the Danish Diet, Cancer and Health cohort that where followed in period of 1993-2006. Based on the addresses of the individuals, monitoring data on NOx, and using exposure modelling, personal estimates on the NOx exposure (as a surrogate for ultrafine particle levels) were made. An increased incidence rate ratio (IRR) for lung cancer of 1.30 [95% confidence interval (CI), 1.05–1.61] for people exposed above 29.7 µg/m^3 NOx (upper quartile) compared to people exposed below 17.2 µg/m^3 NOx (lower quartile), and an increased IRR of 1.21 (95% CI, 0.95–1.55) for lung cancer in association with living within 50 m of a major road (> 10 000 vehicles/day). The results showed tendencies of stronger associations among non-smokers, among those with a relatively low fruit intake, and among those with a longer school attendance.

Also the associations between exposure and occurrence of other type of cancer forms were examined in this cohort. In this analysis significant association for occurrence of cervical cancer and brain cancer was found, however, this was concluded as a finding that needed be further verification Raaschou-Nielsen et al (2011b).

Raashou-Nielsen et al. (2012) from the same cohort as above found that mean levels of NO2 at the residence since 1971 were significantly associated with mortality from cardiovascular disease (Mortality Rate Ratio, 1.26; 95% Confidence Interval: 1.06–1.51), per doubling of NO2 concentration) and all causes mortality (MRR, 1.13; 95% CI, 1.04–1.23, per doubling of NO2 concentration) after adjustment for potential confounders. For participants who ate less than 200 g of fruit and vegetables per day, the MRR was 1.45 (95% CI, 1.13–1.87) for mortality from cardiovascular disease and 1.25 (95% CI, 1.11–1.42) for mortality from all causes.

It was concluded that long term exposure to traffic air pollution in Denmark is associated with mortality from cardiovascular diseases and all-cause mortality, after adjustment for traffic noise. The association was strongest for people with a low fruit and vegetable intake.

Further, Raashou-Nielsen (2013a) followed 52 061 persons from the Danish Diet, Cancer and Health cohort for diabetes-related mortality from 1993–1997 and up to the end of 2009. Residential addresses were traced and front door concentrations of NO2 (as an indicator of traffic related air pollution) were estimated using The Danish AirGIS dispersion-model and using data on the proximity to the measuring stations, traffic density, dimensions of buildings, distance to roads etc. It was found that mean levels of NO2 at the residence since 1971 were significantly associated with mortality from diabetes. Exposure above 19.4 µg/m^3 (upper quartile) was associated with a mortality rate ratio (MRR) of 2.15 (95% CI 1.21, 3.83) when compared with below 13.6 µg/m^3 (lower quartile), corresponding to an MRR of 1.31 (95% CI 0.98, 1.76) after adjustment for potential confounders, i.e. and increased risk of 31% per 10 µg/m^3 NO2. Thus, the study suggested that long term exposure to traffic related air pollution is associated with mortality from diabetes.

The DCE (2014) report is a recent Danish review on the health impact from the air pollution in Denmark. This review in its impact assessment very much relies on the most recent international epidemiological data and reviews (as well as the Danish studies) and the dose-response relationships derived in these studies.

Specific attention in the report is given to the updated dose-response analysis in relation to long-term studies provided by Hoek (2013), Table 2-5.

TABLE 2-5 MORTALITY RISK ESTIMATES, LONG-TERM EXPOSURE STUDIES AS COMPILED BY HOEK ET AL. (2013).(DCE 2014)

Health outcome	PM_{10} per 10 µg/m^3	$PM_{2.5}$ per 10 µg/m^3	EC/BC per 1 µg/m^3	NO_2 per 10 µg/m^3
Total death	3.5% (0.4%-6.6%)	6.2% (4.1%-8.4%)	6.1% (4.9%-7.3%)	5.5% (3.1%-8%)
Cardiovascular death	2%-8% ($PM_{10-2.5}$)	15% (4%-27%)	4%-11%	-2%-36%
Respiratory death	4%-67%	2.9% (-6%-13%)	11%	3%-197%

These figures indicate that per µg/m^3 EC/BC is associated with a 10 times larger response compared to PM2.5. However, when discussing this it was emphasised that the epidemiological data at present is too limited in order to describe more precise an independent effects of EC/BC (as well as for particle number) compared to the effects from PM2.5.
Overall, based on the current evidence it was estimated that the PM (and especially PM2.5) by far contributes mostly to the adverse health outcome from air pollution in Denmark. Based on 2011 PM2.5 levels it was estimated that the air pollution on an overall basis could be associated to 3400 extra deaths in Denmark.

2.4.5 Recent European data, ESCAPE

The effects on long-term exposure to air pollution in Europe are assessed in the European ESCAPE project (European Study of Cohorts for Air Pollution Effects) conducted during the period 2008-2012. In the sub-projects individual exposure estimations were made using the people's addresses, data from air monitoring stations, and using air pollution distribution models taking into account data on local geographical variables and the traffic intensity.

Beelen et al. (2013) reported data in connection with the ESCAPE project on mortality in relation to long term exposure from 22 European cohort studies (including a cohort from Denmark) covering a total study population of 367 251 participants who contributed with 5 118 039 person-years at risk (average follow-up 13·9 years). In the period 29 076 died of natural causes. From a meta-analysis of these data a significantly increased hazard ratio (HR) for all-cause mortality of 1.07 (95% CI 1·02–1·13) was recorded in relation to an increase in PM2·5 of 5 μg/m³.
HRs for PM2·5 remained significantly raised even when only including participants exposed to pollutant concentrations lower than the European annual mean limit value of 25 μg/m³ (HR 1·06, 95% CI 1·00–1·12) or below 20 μg/m³ (1·07, 1·01–1·13).
It is remarkable that these European data indicate a 2.3 times higher relative risk compared to the US cohorts from which the WHO dose-response assessments has been established. This higher potency of PM2.5 may be due to some differences in design as the ESCAPE study used within area variation of the PM2.5 instead of between area variation in the PM2.5. This in combination with the modelled personal exposure estimates may give a more precise description of the exposure of the individuals leading to higher risk estimates in relation to the adverse effects.

In a subsequent study Beelen et al. (2014) analysed the cohorts with respect to cardiovascular mortality. In the cohorts a total of 9994 died due to cardiovascular diseases. On an overall basis the hazard ratios for total cardiovascular mortality, ischemic heart disease deaths and myocardial infarction death were very close to 1 for all pollutant measures. Only for death in relation to cerebrovascular diseases a non-significant increased HR of 1.21 (0.87-1.69) was found in association with an increase in PM2·5 of 5 μg/m³.

Rouschou-Nielsen et al. (2013b) reported a prospective analysis on lung cancer from 17 cohort studies based on data from nine European countries. Exposure levels were modelled in relation to addresses and estimates were made for PM10, PM2.5, coarse PM $_{(PM10 - PM2.5)}$, soot (PM2.5 absorbance), nitrogen oxides, and two further traffic indicators. Overall 312 944 cohort members contributed with a total of 4 013 131 person-years at risk. During the mean follow-up period of 12.8 years, 2095 lung cancer cases were diagnosed. The meta-analyses showed a statistically significant association between risk for lung cancer and PM10 (hazard ratio HR= 1.22 (95% CI 1.03–1.45) per 10 μg/m³). For PM2.5 the HR was 1.18 (0.96–1.46) per 5 μg/m³. Identical HRs in relation to PM10 and PM2.5 were found for adenocarcinomas of the lung (1.51 (1.10–2.08) and 1.55 (1.05–2.29), respectively).
An increase in road traffic of 4000 vehicle-km driven per day within 100 m of the residence was associated with an HR for lung cancer of 1.09 (0.99–1.21). The results showed no association between lung cancer and nitrogen oxides concentration (HR= 1.01 (0.95–1.07) per 20 μg/m³) or traffic intensity on the nearest street (HR= 1.00 [0.97–1.04] per 5 000 vehicles per day).

For non-malignant respiratory mortality, however, Dimakopoulou et al. (2014) did not find any association related to air pollutants including PM2.5. This study was performed with 16 cohorts with a total of 307 553 subjects for which exposure estimations was done based on measurements in the period 2008-2011.

Cesaroni et al. (2014) reported data from ESCAPE on the incidence of acute coronary events (myocardial infarction and unstable angina) from 11 European cohorts (including a cohort from Denmark) covering more than 100 000 people. The participants were in-rolled in the cohorts in the period 1997 to 2007 and followed for an average of 11.5 years. A total of 5 157 participants experienced incident coronary events. An increase of 5 μg/m³ in the annual PM2.5 level was associated with a 13% increased risk of coronary events (hazard ratio 1.13, 95% confidence interval 0.98 to 1.30), and an increase of 10 μg/m3 in the annual PM10 level was associated with HR of 1.12 (1.01 - 1.25). Positive but non-significant associations were found for other pollutants.

Wang et al. (2014) studied the associations between long-term exposure to metallic constituents in the PM10 and PM2.5 fractions and cardiovascular mortality in 19 European cohorts covering 322 291 inhabitants and 9 545 cardiovascular deaths. Eight elements were measured for in the PM2.5 and PM10 samples: copper (Cu), iron (Fe), potassium (K), nickel (Ni), sulfur (S), silicon (Si), vanadium (V) and zinc (Zn). These metals reflected major anthropogenic sources such as road traffic non tailpipe emissions including brake linings (Cu, Fe, Zn), tire wear (Zn), industrial (smelter) emissions (Fe, Zn), crustal materials (Si, K), fossil fuel combustion (Ni, V, S) and biomass burning (K). Three two-week measurements of PM2.5 and PM10 were conducted during different seasons between October 2008 and May 2011 at 20 sites (except in The Netherlands 40 sites) in each cohort study area (1 year per study area). Annual average concentrations of PM constituents were obtained by adjusting temporal variation measured at continuous background sampling sites in each study area in the entire period.
Based on a combined analysis of the 19 cohorts, no statistically significant association was found between long-term exposure to the 8 elemental constituents of the PM2.5 or PM10 fractions and total cardiovascular mortality.

Overall, the studies conducted in connection with the ESCAPE project indicate increased all-cause mortality in relation to long-term exposure to PM2.5 (an increase in mortality of 7% per 5 μg/m^3 of PM.2.5) and an increased risk for lung cancer (an increase of 18% per per 5 μg/m^3 of PM.2.5). However, no association could be found between PM2.5 exposure and increased risk for mortality from cardiovascular diseases or from respiratory non-malignant diseases. Also when looking at metallic elements in PM2.5 and PM10, no significant association could be found between exposure to the metals and cardiovascular mortality.
An increase of 13% was found for the incidence of acute coronary events (fatal as well as non-fatal) per 5 μg/m3 of PM.2.5.

2.4.6 Dose-response estimates for ultrafine particles; EC, or black carbon

Overall, four studies have found that make estimations regarding dose-response assessments for either ultrafine particles, elemental carbon, or black carbon (Hoek et al., 2010, Janssen et al., 2011, Hoek et al., 2013 and Vermeulen et al., 2014)

Although specific data are lacking for more precise dose –response estimations, a first attempt to make an expert based estimate of the dose response relationship between urban air levels of ultrafine particles and mortality and hospital admissions was undertaken by Hoek et al. (2010). Data included five epidemiological studies on ultrafine particles and mortality, four for respiratory hospital admissions and five for cardiovascular hospital admissions. Further, epidemiological studies assessing the impact of living near major roads were included as proximity to major roads may be used as an indicator for exposure to ultrafine particles. From an overall analysis of these data a long-term increase of 1000 particles/cm^3 was estimated to be associated to an increased mortality rate of 0.3% (range 0.1-1.2%). This estimate for ultrafine particles may be compared to the findings that 1 μg/m^3 of PM2.5 is associated to a 0.6% increase in mortality.

Janssen et al. (2011) examined to which extent the adverse health effects from PM2.5 could be ascribed to combustion related black carbon particles (BCP) (measured as either black smoke (BS), black carbon (BC), elemental carbon (EC) or absorbance (Abs)). From review of the literature it was found that a relatively large part 40-70% of the roadside PM2.5 increment above background level is to be attributed to BCP.
For making comparison EC was used as a measure for BCP. A relation from black smoke measurements BS, of 10 μg/m^3 BS = 1.1 μg/m^3 EC was used, as this relationship was found from the average from 11 studies including both measures.
When studying acute effects from time-series studies the effects (daily mortality or number of hospital admissions) per 1 μg/m^3 (averaged over 24-hours) were generally one order of magnitude higher for the BCP measure compared to the PM2.5 measure. However the magnitude of the effects

analysed on the basis of interquartile differences of the pollutants levels were rather similar for PM2.5 and BCP. However, when using two-pollutant models on the data from these studies it was found that the effect of BCP was more robust than the effects of the PM metric.
From a analysis 4 long-term mortality studies it was found that per 1 µg/m^3 (as annual average) the effects of EC was 5-14 times higher for all-cause mortality than for the PM2.5 metric.
Based on these results it was concluded that BCP is a valuable indicator of the health risks of air quality dominated by primary combustion particles.

Hoek et al. (2013) made on update on the dose-response relationship in relation to mortality from long-term exposure. In relation to the assessment of PM2.5 and PM10 dose responses Hoek et al. (2013) identified 18 publications of which 16 were published since the WHO analysis. Based on a pooled analysis of these studies an overall estimate of the dose-response was estimated. From this an increase in 10 µg/m^3 PM2.5 was associated with an increase in all-cause mortality of 6%; an increase in 11% for cardiovascular mortality, and an increase of 3% for non-malignant respiratory diseases. All causes mortality was also associated with elemental carbon (an increase of 6% per 1 µg/m^3 elemental carbon) and NO2 (an increase of 5% per 10 µg/m^3 NO2), both of which was considered as markers of combustion sources.

Vermeulen et al. (2014) assessed the dose-response for lung-cancer in relation to diesel exhaust from an analysis of three occupational cohort studies on diesel exhaust. Using measured data on elemental carbon and making extrapolation from occupational exposure to lifetime exposure to the general population an increased risk of cancer of 5% was found for an increase in elemental carbon of 0.8 µg/m^3. Thus for lifetime environmental exposure to 0.8 µg/m^3 of elemental carbon a number of 21 excess lung cancer deaths was estimated to occur among a population of 10 000 people. Based on this it was estimated that approximately 6% of all annual lung cancer deaths in the US may be due to diesel exposure.

Based on the data presented above an overview of the dose-response associations can be given, Table 2-6.

TABLE 2-6 OVERVIEW OF DOSE-RESPONSE ASSOCIATIONS FOR FINE AND ULTRAFINE PARTICLES

Effects	Increased response				References
	PM2.5 (1 µg/m^3)	EC (1 µg/m^3)	BS (1 µg/m^3)	Number conc. (1000 µg/cm^3)	
Mortality, long-term exp	0.6%			0.3%	Hoek et al., 2010
Mortality, long-term exp	0.7%	6%			Janssen et al., 2011
Mortality, short-term exp	0.048%		0.068%		Janssen et al., 2011
Mortality, long-term exp	0.6%	6%			Hoek et al., 2013
Lung cancer		6%			Vermeulen et al., 2014

2.5 Overall, exposure and risk in relation to ultrafine particles

From the review above it can be highlighted that the mass based fraction of measured ultrafine particles in ambient air is relatively small compared to the mass based metrics for PM10 and PM2.5 which are the standard metrics for ambient air particulate matter measurements. E.g. Gugamsetty et al. (2012) found that ultrafine particles on a mass basis (PM0.1) contributed with 1.4 μg/m^3 (or 6.4%) of the PM2.5 level of 21.8 μg/m^3 in an urban area in Taiwan.

This correlates with the data from Geller et al. (2002) that measured PM0.1 levels of 1.20 μg/m^3 and 0.74 μg/m^3 at sites with high and more moderate traffic density. The levels were associated to a particle number concentration of 2.5 x 10^4 particles/cm^3 and 1 x 10^4 particles/cm^3, respectively.

Exposure

In Denmark average (annual) ultrafine particle levels in the range of **4 000-15 000 particles/cm^3** have been found from measurement in rural background and busy urban areas. During a day at specific hot spot locations with heavy traffic peak levels up to 180 000 particles/cm^3 have been reported.

Thus average daily exposure from 24 hours exposure to outdoor ultrafine particles would for an **adult person** with a daily ventilation volume of 20m^3 result in daily exposure of:

4000-15 000 particles/cm^3 x 20 m^3 x 10^6 (cm^3/m^3) = **8-30 x 10^{10} particles per day**
or for a person weighing 70 kg exposure would be **1-4 x 10^9 particles/ kg day.**

For **small children** the exposure is higher as their inhalation rate is inhalation increased compared to adult. Thus children (1-5 years old) inhaling 0.5 m^3/kg/d would be exposed to:
4 000-15 000 particles/cm^3 x 0.5 m^3/kg/day x 10^6 (cm^3/m^3) = **2 – 7.5 x 10^9 particles/kg/day.**

It has however to be noted that such exposure figures only gives indication of the exposure level to free ultrafine particles, and that a large fraction of particles above 100 nm in the PM2.5 fraction is due to agglomerated ultrafine particles primarily from the combustion related sources. Thus, in urban area about 1/3 of the average PM2.5 level at about 18-20 μg/m^3 is due to these combustion related fractions (see Figure 2-6).

Therefore, it can be assumed that about 30% of the overall PM2.5 exposure may be due to free but mostly agglomerated ultrafine particles. This would equal an average exposure to ultrafine particles or agglomerates thereof of about of about **5-6 μg/m^3**.

Assuming a daily ventilation rate of 20 m^3 for an in urban environment, this would lead to a daily exposure to **100-120 μg/day**. For an **adult person** of 70 kg, a daily inhalational dose of up to **1.4-1.7 μg /kg bodyweight/day** may be assumed.

Thus children (1-5 years old) inhaling 0.5 m^3/kg/d would be exposed to:
5-6 μg/m^3 x 0.5 m^3/kg/d ay= **2.5-3 μg /kg bodyweight/day.**

Effects and dose response relationship

There is a general consensus in literature that the toxicity of PM2.5 to a great extent is driven by the combustion related constituents (e.g. from traffic exhaust and wood burning) and thus that a steeper dose-response apply for this fraction compared to the remaining fractions in PM2.5. A more precise and independent dose- response relationship for the combustion derived and ultrafine derived fraction has however not been determined.

In order to avoid exaggeration of the effects from the ultrafine particles it may be assumed that the at least the same dose-response relationship as found for PM2.5 apply (see Table 2.5 and Table 2.6).

On the other hand if it is assumed that 1/3 of the PM2.5 levels pertain to ultrafine particles (free+ agglomerated) and that this fraction 100% drives the health impact this would then call for a 3 times higher dose-response estimate compared to the current estimate for PM2.5.

In the recent report DCE (2014) providing an overall health impact assessment of the air pollution in Denmark (from all anthropogenic as well as natural sources, and from national sources as well as PM coming from abroad) has been made. The following table indicates additional cases of health outcomes based on primarily the levels of PM2.5 in Denmark. The data is based on exposure modelling for the whole Danish population and dose-response relationships for the PM2.5 exposure.

TABLE 2-7. ESTIMATED NUMBER OF VARIOUS NEGATIVE HEALTH OUTCOMES IN DENMARK (2011) DUE TO MAINLY AMBIENT PM2.5 EXPOSURE OF THE POPULATION (DCE 2014)

Adverse health effects	2011 - Estimated cases -
Chronic bronchitis	3 300
Days with reduced activity (sickness days)	3 380 000
Hospital admissions, Respiratory diseases	179
Hospital admissions, Cerebro-vascular diseases	416
Cardiac failure	285
Lung cancer	506
Use of bronchodilatators, children	88 800
Use of bronchodilatators, adults	647 000
Cough episodes, children	307 000
Cough episodes, adults	666 000
Episodes with deep pulmonary symptoms, children	215 000
Episodes with deep pulmonary symptoms, adults	240 000
Mortality, acute exposure	142
Mortility, long term exposure	3 330
Years of life lost (YOLL)	35 300
Infant mortality	4

In conclusion and as the table indicates there are substantial negative health effects associated to ambient PM2.5 in Denmark. This is most clearly expressed by the estimated 3 330 annual cases of mortality which corresponds to just above 5% of the yearly mortality rate in Denmark. At least 1/3 of these cases may be considered to be associated to the exposure to ultrafine particles (i.e. the free fraction plus the agglomerated fraction made up by ultrafine particles).

3. Indoor air

3.1 Indoor levels of ultrafine particles

3.1.1 Indoor particle number concentrations

Several studies have used mobile devices for measuring ultrafine particles and particle numbers in the indoor environment. In these studies the levels are measured in different locations in different situations and during different activities. In the following the information from these types of studies will be used for describing the contribution to ultrafine particles in the indoor environment from the various sources.

In a study in 56 Danish homes Bekö et al (2013) reported a geometric mean of 22.3 x 10^3 particles/cm^3 was measured during the period when the occupants were awake. During sleep and when the homes were vacant the mean level was below 6.1 x 10^3 particles/cm^3.
A very high variation in the 24-hours average levels was found, ranging from about 1500 particles/cm^3 to 251 000 particles/cm^3 for the geometric means. At the high exposure levels 97% of the particles were due to the use of candles.
The overall average mean for the integrated 24 hours exposure was calculated to 334 x 10^3 particles (h /cm^3 day). The average particle diameter was found to 76 nm with only 5% of the measured particles above 120 nm.

This high variation indoors indicates the importance of indoor sources affecting the indoor environment.

Afshari et al. (2005) in a full scale test chamber setting examined the contribution of various indoor sources/activities to the levels of ultrafine particles in indoor air. For 13 activities the following levels of ultrafine particles were found in the full scale test chamber, see Table 3-1.:

TABLE 3-1 PARTICLE LEVELS (NUMBER CONCENTRATIONS) MEASURED DURING 13 ACTIVITIES IN A TEST CHAMBER (AFSHARI ET AL. 2005)

UFP source	C_{max}(particles/cm^3)
Flat iron (without steam) on a cotton sheet	550
Flat iron (with steam) on a cotton sheet	7 200
Air-freshener spray	29 900
Scented candles	69 600
Pure wax candle	241 500
Electric stove	111 500
Radiator	218 400
Vacuum cleaner with full bag	21 400

UFP source	C_{max}(particles/cm^3)
Vacuum cleaner (motor) without bag	38 300
Cigarette	213 300
Gas stove	79 600
Heater	116 800
Frying meat	150 900

As can be seen the highest levels were achieved in relation to candle burning, whereas using a radiator, cigarette smoking and frying meat also contributed with very high levels (all above 150 000 particles/cm^3).

From this it is evident the personal exposure to ultrafine particles due to many hours spend in the home would very much depend on which type of activities and indoor sources for the emission of ultrafine particles that is represented in the home.

Bekö (2013) described the relative exposure to ultrafine particles from the various indoor sources in a study with measurement from 58 Danish homes. As indicated in Table 3-2 candle burning and cooking/ toasting are very significant sources for the daily indoor exposure.

TABLE 3-2 SUMMARY OF THE OCCURANCE, DURATION AND CONTRIBUTION TO TOTAL RESIDENTIAL EXPOSURE OF THE ANALYSED SOURCE EVENT BEKÖ (2013)

Activity type	No. of events analysed (-)	No. of homes with the event (-)	Average daily source duration (min/d)	Average duration of increased PN level per event (h)	Average contrib. to the total residential integr. exposure (%)
Cooking	60	37	35	5.2	29
Toasting	14	12	15	3.6	11
Candle burning	39	28	142	8.2	58
Special events	4	3	51	6.2	22
Unknown	118	52	50	3.0	14
Window opening	14	11	30	2.3	3

However, also other indoor environments may contain very high level of ultrafine particles. Wallace and Ott (2011) measured the indoor levels in 22 restaurants and reported mean average levels over a duration of 27-128 minutes in the range of 10 000 – 228 000 particles/cm^3 with a reported peak exposure level of about 340 000 particles/cm^3.

Section 3.2 provides further insight to some of the sources for ultrafine particles in the indoor air.

3.1.2 Indoor particle mass concentration

Mass concentration for particulate matter has mainly been given as a measure of fine particles, PM2.5, thus this fraction also contain agglomerates of ultrafine particles.

DFGU (2008) in an overview of PM2.5 levels in indoor air provide the following data on typical (average) indoor PM2.5 levels in Germany:

Indoor, homes:	20-30 µg/m^3
Restaurants/cafés:	178 µg/m^3
Pubs/Kneipen:	200 µg/m^3
Discoteques:	808 µg/m^3

Smoking may result in much higher levels: levels up to 1400 µg/m^3 and about 7000 µg/m^3 were measured in pubs and discotheques, respectively.

In 21 flats in Copenhagen in which couples of aged people (non-smokers) were living a mean level of 12.6 µg/m^3 PM2.5 and a mean number of 19,016 particles/cm^3 were measured (Bräuner et al., 2008).

Raashou-Nielsen et al. (2011) reported a mean PM2.5 levels of 17-22µg/m^3 (5-95% range of 5.7-58 µg/m^3) based on 1122 measurement in the bedrooms of 389 infants in rural and urban areas. Especially smoking, use of fireplace, stove and candles increased the bedroom PM2.5 levels as well as absorbance measurements of black smoke.

3.2 Sources for indoor ultrafine particles

3.2.1 Candle light

The use of candle lights is a very important source of ultrafine particles in indoor environment, and often the most important source for ultrafine particles in indoor air.

In a recent study by Bekö et al. (2013) the levels of ultrafine particles were measured in 56 Danish homes and followed during a period of 45 hours. Ultrafine particles were measured with a Nanotracer PNT1000 device giving information on particles numbers and the particle diameters. During burning of candles, especially the levels of particles with diameters in the range of 20-35 nm peaked. Levels up to nearly 1 million particles/cm^3 were measured when using candle lights. Candle burning was used in half of the homes in general and accounted for 58% of the total daily integrated exposure to ultrafine particles of 3.3 x 10^5 particles/cm^3 x hour/day.

Pagels et al. (2009) investigated the physical and chemical properties of candle smoke particles in a full chamber experiment. The authors found that during steady burning conditions a high number of ultrafine particles, where emitted. Due to the chemical composition, mainly phosphates and alkali nitrates, the authors concluded that the particles were derived from flame retardants in the wick (Pagels et al., 2009). The particle size distribution ranged from 16 to 1000 nm, with a peak around 20 to 30 nm. During sooting burning conditions larger particles mainly consisting of elemental carbon were emitted. During sooting burn the particle size increased to a geometric mean diameter of 270 ±30 nm. When candles were extinguished, and during the following smouldering phase, the emitted particle size increased from the initial 20-30 nm to 335±30 nm, and the composition of the particles changed from elemental carbon and inorganic matter to primarily organic matter (Pagels, 2009). The chemical composition of the organic particles was not further described.

Also Afshari et al. (2005) found that candle burning among various indoor sources lead to the highest concentrations of ultrafine particles in indoor air. In an experimental full scale exposure chamber a level of 241,000 particles/cm^3 was measured.

Chaung et al. (2012) determined the emission rate of PM2.5 from various types of combustion in test chamber experiments. For candles emissions rates up to 23 mg PM2.5 per g candle were estimated. It should be noted, however, that for incense used e.g. during church services an emission rate of up to 417 mg PM2.5/g incense was estimated.
In UK in a church during mass PM2.5 levels up to 1300 µg/m^3 were measured during use of candles and incense at the same time.

3.2.2 Tobacco smoke particles

Tobacco smoke is one of the major sources of human exposure to ultrafine particles in the indoor environment. Ning et al. (2006) studied the contribution of ultrafine particles by different numbers and brands of cigarettes. They found that the geometric mean diameter of the generated particles was approximately 150 nm. After smoking a cigarette during 5 minutes in a 30 m^3 chamber the level of 150 nm particles increased from 2.5 x 10^3 particles /cm^3 to 90 x 10^3 particles /cm^3.

Semple et al. (2012) in his study regarding use of different solid fuels and their contribution to ultrafine particles in indoor air of the home (see below) found that resident smoking was the dominant source to ultrafine particles contributing with an average level of ultrafine particles of 99 µg/m^3.

Afshari et al. (2010a) studied the infiltration of ultrafine particles from smokers flat into non-smokers flat, and found that up to 9% of the generated particles from smoking could be transferred to receiving flats. In the studies by Ning et al. and Afshari et al., no further chemical characterization of the particles were performed.

Böhlandt et al. (2012) described the effect of Environmental Tobacco Smoke (ETS) on the concentration of metals in indoor air, and found that median levels of cadmium were 0.1 ng/m^3 for non-smokers and 0.8 ng/m^3 for smokers' households. Median concentrations of cerium were 0.4 ng/m^3 and 9.6 ng/m^3, and median concentrations of lanthanum were 0.2 and 5.9 ng/m^3, for non-smokers and smokers, respectively (Böhlandt et al., 2012).

Slezakova et al. 2013 studied the concentration of particle-bound PAHs in indoor air, and found that in smoker homes the mean total concentration of 18 PAHs studied was 17.1 and 16.6 ng/m^3 in PM10 and PM2.5, respectively. The corresponding concentrations in non-smoking homes, were 2.3 times lower, with means of 7.6 and 7.2 ng/m^3, for PM10 and PM2.5, respectively.

These two studies therefore indicated that ETS particles contribute with exposure to organic carbon (including PAHs) and metals, such as cadmium, cerium and lanthanum.

3.2.3 Cooking

Vinzents et al. (2005) studied the concentration of ultrafine particles in the breathing zone in 15 young and healthy volunteers in Copenhagen using portable instruments for measuring particle number concentrations. As can be seen from Figure 3-6 the highest peak exposure during a day pertain to cooking where the exposure reached a level of about 350 000 particles/cm^3.

Buonanno et al. (2014) concluded on the basis of a personal exposure study, that women were exposed to higher numbers of ultrafine particles due to cooking activities, than men. They calculated the daily average personal exposure for women to 1.8 x 10^4 /cm^3 and 2.9 x 10^4/cm^3 for summer and winter, respectively. This compared to a full time working male; 9.2 x 10^3/cm^3 and 1.3 x 10^4/cm^3, also for summer and winter, respectively.

Bekö et al. (2013) studied the daily variation in the concentration of ultrafine particles, and found that the concentration of ultrafine particles in indoor air peaked during cooking events. Cooking in 37 Danish homes represented on average 43% of the daily indoor exposure to ultrafine particles.

Series of cooking events, and the resulting release of UFP, were described by Dennekamp et al. (2001). They found that the release of particles from cooking was related to the method applied. The heat source alone gave rise to a significant release of UFP, either gas or electric heating, with 26,000 to 94 000 UFP/cm^3, respectively. The highest release of UFP observed by Dennekamp et al. (2001) was by frying bacon on gas heating, which gave rise to a particle level of 590 000 UFP/cm^3.

Zhang et al. (2013) studied the emission of ultrafine particles from microwave popcorn, and found that the emission of ultrafine particles was related to both flavour and the energy intensity that were used. The emission rates of ultrafine particles ranged from 1.9 x 10^{10} to 8.0 x 10^{10} particles/min. Ultrafine particles and PM2.5 generated by microwaving popcorn were 150-560 and 350-800 times higher than the emissions from microwaving water, respectively.

The studies mentioned above do however not consider the chemical characteristics of the particles generated during the cooking events.

Torkmahalleh et al. (2012) determined the emission PM2.5 rates from various types of cooking oil when heating. Lowest emission flux of 6.1 x 10^5 µg PM2.5/min/m^2 was found for soybean oil whereas the highest flux of 5.7 x 10^6 µg PM2.5/min/m^2 was found for olive oil. The lowest particle number flux of 3.5 x 10^{13} particles/ min/m^2 was determined for soybean oil, and the high particle number flux of 3.8 x 10^{14} particles/ min/m^2 was determined for peanut oil. The major particle mode sizes were in the interval of 25 nm to 82 for the various oil and 76-99% of the particles were within the nanoparticle size (<100 nm).

3.2.4 Fire place/ wood burning

Solid fuel combustion has been documented to be a significant source of ultrafine particles in ambient air. Semple et al. (2012) studied several different solid fuels and their contribution to indoor air ultrafine particles. One hundred homes were studied in Ireland and Scotland. Solid fuels, such as coal, wood and peat gave rise to time-weighted-average levels of ultrafine particle indoor between 6 and 11 µg/m^3, compared to gas cookers, 7 µg/m^3. In homes with at least one resident smoker, an average level of 99 µg/m^3 was reported. Conclusively burning of fossil fuel results in significant ambient UFP, where the effect on indoor air is quite limited, compared to smoking.

The indoor levels of *ultrafine particles* have been measured in Denmark during winter for seven selected homes equipped with modern wood stoves. Very different levels were measured and the lowest level (considered comparable to outdoor background level) of 5 x 10^3 particles/cm^3 was found in a home with a stove using indoor air for the combustion. In two other homes levels of 2.2-2.3 x 10^5 particles/cm^3 were measured. The levels were considered very much to depend on a multitude of factors for affecting the air flow indoors e.g. the construction of the house, the stove, the chimney and also very much to depend on the occupants´ way of igniting the stove. (Afshari et al., 2010b; Danish EPA 2012).

3.2.5 Electric devices

Afshari et al. (2005) reported the following levels of ultrafine particles measured using a condensation particle counter in indoor air in a test chamber with connection with the different uses of electric devices:

Flat iron without steam:	550 particles/cm^3
Flat iron with steam:	7 200 particles/cm^3
Electric stove:	111 500 particles/cm^3

Vacuum cleaner with full bag:	21 400 particles/cm^3
Vacuum cleaner without bag:	38 300 particles/cm^3

Wallace and Ott (2011) measured the levels of ultrafine particles using a condensation particle counter in indoor in two homes. Using electric devices the following levels were reported as 1-hour average values:

Electric toaster:	99 000 particles/cm^3 (peak: 174 000 particles/cm^3)
Electric toaster oven:	7 000-144 000 particles/cm^3
Electric stove:	6 000-145 000 particles/cm^3
Curling irons:	5-193 000 particles/cm^3
Steam iron:	10 000-81 000 particles/cm^3
Hair dryers:	0-137 000 particles/cm^3
Hair straightener:	16 000 particles/cm^3
Laser printer:	68-4200 particles/cm^3
Vacuums:	310-3500 particles/cm^3

Laser printers and hard copy devices have been demonstrated to release significant amounts of ultrafine particles to the indoor environment. Thus, Tang et al. (2012) measured up to 23 600 UFP/cms3 in an office room during a printing phase of a laser printer whereas Salthammer et al. (2012) reported short peak levels of 60,000-100,000 particles/cm3 during laser printing.

3.3 Overall exposure considerations from indoor air

As indicated above the personal exposure to ultrafine particles very much depends of the daily activities of the person, e.g.:

- Time spend outdoors in various out door environments
- Time spend indoors in various indoor environments
- Duration of various activities of the person
- The ventilation rate of the person

Thus the best method for having a measure for the daily and average exposure is to ultrafine particles would be data from person borne measurement for 24 hours during various periods that will represent a whole year and activity pattern of a person.

The great variation in daily exposure can be seen from the data by Bekö et al. (2013) that measured indoor levels of ultrafine particles continuously for 45 hours in 56 Danish homes in the period from October to February.

An overall mean 24 hour exposure level 15,600 particles/cm^3 was calculated and a mean integrated exposure level of 334 000 particles (hour/cm^3 day) was found.

Thus, for **an adult person** inhaling 20m^3 per day, this would result in a daily inhalation of:
334 000 particles (hour/cm^3 day) x 20m^3/24 hour/day x 10^6 (cm^3/m^3) = **2.8×10^{11} particles/day** or about **4×10^9 particles/kg bodyweight/day** for a person weighing 70 kg.

Small children (1-5 years old) inhaling 0.5 m^3/kg/d would be exposed to:
334,000 particles (hour/cm^3 day)/24 hour/day x 0.5 m^3/kg/day x 10^6 (cm^3/m^3) = **7×10^9 particles/ kg/ day.**

The composition of the various fractions of the ultrafine particle exposure may vary a lot depending of the source. However, very little has been found on measurements of the chemical content of the ultrafine particles. The contribution from various sources/activities under representative conditions can be found in Table 3-1.

With respect to mass based exposure estimate to ultrafine particles + agglomerates thereof this estimate may be based on typical indoor PM2.5 levels of 20-30 μg/m^3 as indicated from the German data. The Danish data is from flats with aged people and therefore considered to be less representative for an average population exposure.
If it is assumed – as for the ambient air particles- that 1/3 of this level stems from ultrafine + agglomerated ultrafine particles this would correspond to an exposure level of **7-10 μg/m^3**.

If **an adult person** daily inhales 20 m^3 air, this would result in a daily exposure of **140-200 μg/m^3 of ultrafine particles**. With a bodyweight of 70 kg this would correspond to **2-3 μg/kg/day**.

Small children (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to 7-10 μg/m^3 x 0.5 m^3/kg/day = **3.5-5 μg/kg/day.**

3.4 Health effects of ultrafine particles in indoor air

In general there is a very sparse data base on indoor ultrafine particles or PM2.5 and adverse health effects. As indicated below hazard and risk assessment of indoor particulate matter is therefor based on the data from particulate matter in ambient air, as ambient air PM significantly contribute to the indoor air. However, it has to be noted that additional sources exist for the indoor environment as described above but data are lacking to account for these differences when making hazard and risk evaluations.

Recently the Norwegian Folkehelseinstituttet has made a review on indoor air pollutants including particulate matter in order to make recommendations with respect to guidelines values for the pollutants. It was acknowledged that the database on the adverse effects on indoor particles is very poor both in relation to PM2.5 and in relation to the data on the health implication of ultrafine particles. Therefore assessment was based on the data base on PM2.5 in ambient air and the WHO (2006) evaluations. Based on this an air indoor guidance PM2.5 values of 8 μg/m^3 as an annual mean and 15 μg/m^3 as a 24 hour mean were recommended (Folkehelseinstituttet 2013).

Also the Irish EPA (2013) and WHO (2012b) in recent reports assessed the health impact of PM2.5 from indoor combustion sources. Health impact assessments were in these studies to some extent based on the data on ambient air dose-response for PM2.5.

Below a few specific studies are mentioned:

-In a review by Wichenthal et al. (2007) on effects from indoor ultrafine particles no specific epidemiological data was found on this issue. However, *in-vitro* and *in vivo* data on ultrafine particles indicated concern, as ultrafine particles *in vitro* were found to be strong sources of oxidative stress and inflammation in the lung and further *in vivo* animal testing suggests that immune responses characteristic for asthma were promoted (the ID of the ultrafine particles were not further specified)

Bräuner et al. (2008) examined the vascular function (microvascular function measured as the digital peripheral tone artery tone of the arm) in 21 couple of elderly people in Copenhagen before and after reduction of the indoor particle levels by filtration. The mean particle level of the non-filtered air in the homes was determined to 12.6 μg PM2.5/m^3 with a mean particle number of

10,016 particles/cm^3 (range 10-700 nm). After filtering the air for 48 hours the particle levels were reduced to 4.7 µg PM2.5/m^3 and 3206 particles/cm^3. After the intervention with air filtering a significant improved microvascular scores both in relation to the PM2.5 and particle numbers were determined, whereas no significant effect was seen in relation to reduction of the fraction of coarse particles (>PM2.5).

-A similar study was conducted by Allen et al. (2011) in an area with a high degree of residential wood burning in Canada, in which 45 healthy persons was tested after a 7 day period with air filtering.
The PM2.5 level was on average reduced from 11.2 µg PM2.5/m^3 to 4.6 µg PM2.5/m^3 and the levoglucosan level (an indicator for wood smoke) was reduced from 127 ng/m^3 to 33 ng/m^3.
The study found that air filtration resulted in improved vascular function and decreased blood concentrations of inflammatory markers suggesting that indoor air particles may play a rule in relation to cardiovascular morbidity.

In conclusion, it is clear that more specific data on the effects on ultrafine particles in indoor air is needed in order to make more precise hazard and risk assessment on the human health in relation to the indoor exposure.

4. Drinking water and soil

4.1 Introduction

Very little data are available regarding measured levels of nanoparticles/nanomaterials in environmental matrices including drinking water and soil. This is partly due to the general lack of suitable analytical methods (including sample preparation techniques) that are sensitive and selective enough to identify and quantify nanoparticles in relevant concentrations, partly due to the complex nature of most environmental matrices and the environmental transformation processes changing the character of the NPs to be studied. Furthermore, it is very difficult with the current analytical methods to distinguish between nanoparticles of anthropogenic ("engineered" NPs) and NP of natural origin.

This situation is generally recognised among nano-researchers and is often stated in scientific reports (e.g. "*the development of monitoring methods for environmental samples is crucial*" (ENRHES, 2009)) and journal articles (e.g. "*…advances in the study….. have been hampered by a lack of adequate techniques for the detection and quantification of ENMs at environmentally relevant concentrations in complex media*" (von der Kammer et al., 2012)). Nowack et al. (2012) state that "*the analytical methods to identify and especially to characterize and quantify ENM at micrograms per liter or lower concentrations in natural systems are not yet available, with the possible exception of fullerenes*".

Therefore, in this section the few data on measured concentrations in drinking water and soil have been supplemented by environmental concentration values predicted by environmental exposure models recently developed for nanomaterials.

4.2 Drinking water

4.2.1 Measurement of nanoparticles/ ultrafine particles

Similar to chemical substances, not only one or a few analytical methods can cover the whole spectrum required to determine NPs in environmental samples including drinking water. However, as some of the most widely used NMs are inorganic and based on metals or metalloids, methods used to identify and quantify such elements in general can also be applied to analysis of NMs, e.g. spectrometric methods such as ICP-MS (inductively coupled plasma mass spectrometry), often in combination with microscopy techniques such as transmission electron microscopy (TEM). Correspondingly, for the organic NMs, analytical methods for chemicals such as liquid or gas chromatography in combination with mass spectrometry (LC-MS or GC-MS) are in principle also applicable to NMs.

The major outstanding issue to be solved in relation to monitoring of NMs in water and other environmental matrices therefore appears to be development of suitable sample preparation techniques ranging from extraction from the matrix, concentration, and fractionation or other separation methods to minimise interference from other materials, dissolved or non-nano-particles of the relevant material while at the same time maintaining the original character of the study object.

4.2.1.1 Surface water

The data available, whether measured or modelled, all regard surface water, which in a large part of Europe is a relevant source of drinking water. Therefore, these data are included in this report.

Boxall et al. (2007) modelled the environmental concentrations of a number of man-made NPs (ENPs) that will occur in surface waters and soils as a result of the use of ENPs in consumer products such as cosmetics, personal care products and paints. Here we have used the result obtained assuming a market penetration of 10%, i.e. the situation where 10% of a product type contains the engineered nanoparticle but Boxall et al. also considered concentrations resulting from market penetrations of 50% and 100%. However, they considered that currently the 10% scenario is the most realistic, but still a conservative scenario.

The ITS-Nano-project (ITS-Nano, 2013) presents a summary of modelled concentrations of TiO_2 in surface waters but also mentions the lack of confirmatory analytical data due to "*the lack of suitable methods for detection and characterisation of nanomaterials when they are embedded in complex matrices including water, soil and food*".

Mueller and Nowack (2008) modelled the exposure to engineered nanoparticles in the environment exemplified by nano silver (nano-Ag), nano titanium dioxide (nano-TiO2) and carbon nanotubes (CNT), based on a substance flow analysis in Switzerland. A "realistic" and a "high emission" scenario were modelled. The matrices modelled included surface waters and soils, see also section 4.3.1.

Sun et al. (2014) modelled predicted environmental concentrations of a number of ENMs for a regional scenario (the EU) and a local scenario (Switzerland) applying a probabilistic method and using the most updated information on ENM production volumes in the EU and in Switzerland. They present the most probable value ("mode value") and its 15% and 85 % percentiles.

Praetorius et al. (2012) have developed an environmental fate model for ENPs and presented the use of the model in a case study of TiO2 nanoparticles in the Rhine River. Their estimated that the TiO2 NP concentration was in the ng/L range (approx. 10^5 particles per liter) in the water compartment taking into account hetero-aggregation with suspended particles in the river.

In their review of the risks posed to surface water-based drinking water by man-made nanoparticles, Tiede et al. (2011) presented, among others, a comparison between modelled $PEC_{surface\ water}$ values for various nano-materials published in recent literature. The PECsw value corresponds to the raw water received at the (drinking) water treatment plant (WTP) assuming 97% removal efficiency at the wastewater treatment plants (WWTPs) prior to discharge. By conventional water treatment the PEC values can typically be reduced by two orders of magnitude while a further significant reduction can be achieved by advanced treatment methods such as membrane filtration.

A summary of the modelling results is presented in Table 4-1, below.

TABLE 4-1 PREDICTED CONCENTRATIONS OF ENGINEERED NANOPARTICLES IN SURFACE WATERS AND SOILS

NM	Water (µg/L)	Soil (µg/kg)	Comments	Reference
Ag	0.010	0.43	UK[1]	Boxall et al., 2007
	0.03-0.08	0.02-0.1	Switzerland, realistic and high emission scenario[2]	Mueller and Nowack, 2008

NM	Water (µg/L)	Soil (µg/kg)	Comments	Reference
	0.588-2.16	-	Conservative and optimistic scenario	Gottschalk et al., 2011 (cfr. Tiede et al., 2011)
	0.66 (0.51-0.94)	-	Europe (most probable + 15% and 85% percentile)	Sun et al., 2014
AlO_3	0.0002	0.01	UK[1]	Boxall et al., 2007
	0.0039	-	Assuming 97% removal of ENP in WWTP	Tiede et al., 2011
Au	0.14	5.99	UK[1]	Boxall et al., 2007
CeO_2	<0.0001	<0.01	UK[1]	Boxall et al., 2007
CNT	0.0005-0.0008	0.01-0.02	Switzerland, realistic and high emission scenario[2]	Mueller and Nowack, 2008
	0.23 0.17-0.35)	-	Europe (most probable + 15% and 85% percentile)	Sun et al., 2014
Fullerenes	0.31	13.1	UK[1]	Boxall et al., 2007
	0.015-0.12	-	Conservative and optimistic scenario	Gottschalk et al., 2011 (cfr. Tiede et al., 2011)
	0.11 (0.07-0.28)	-	Europe (most probable + 15% and 85% percentile)	Sun et al., 2012
	0.0017	-	Assuming 97% removal of ENP in WWTP	Tiede et al., 2011
Hydroxy-apatite	10.1	422	UK[1]	Boxall et al., 2007
Latex	103	4307	UK[1]	Boxall et al., 2007
Organo-silica	0.0005	0.02	UK[1]	Boxall et al., 2007
SiO_2	0.0007	0.03	UK[1]	Boxall et al., 2007
	1.20	-	Assuming 97% removal of ENP in WWTP	Tiede et al., 2011
TiO_2	24.5	1030	UK[1]	Boxall et al., 2007
	0.7-16	0.4-4.8	Switzerland, realistic and high emission scenario[2]	Mueller and Nowack, 2008
	0.015 (0.012-0.057)	.	Europe (median and 15% and 85% percentile)	Gottschalk et al. 2009 (cfr. ITS-nano 2013)

NM	Water (µg/L)	Soil (µg/kg)	Comments	Reference
	0.43-0.14	-	Median; conservative and optimistic scenario, respectively	Gottschalk et al., 2011 (cfr. ITS-nano 2013)
	ng/L-range	-	River Rhine	Praetorius et al., 2012 (cfr. ITS-nano 2013)
	0.53 (0.40-1.4)	-	Europe (most probable + 15% and 85% percentile)	Sun et al., 2014
	4.91	-	Assuming 97% removal of ENP in WWTP	Tiede et al., 2011
ZnO	76	3194	UK[1]	Boxall et al., 2007
	0.008-0.055	-	Conservative and optimistic scenario	Gottschalk et al., 2011 (cfr. Tiede et al., 2011)
	0.09 (0.05-0.29)	-	Europe (most probable + 15% and 85% percentile)	Sun et al., 2014
	1.91	-	Assuming 97% removal of ENP in WWTP	Tiede et al., 2011

1) From use of cosmetics, personal care products and paints assuming 10% market penetration.

2) Not including sludge amended soil, which, according to the authors, is prohibited in Switzerland.

Gottschalk et al. (2013), compare in a recent review the results of modelling studies with analytically measured concentrations for a number of nanomaterials (TiO_2, Ag, ZnO, CNT, fullerenes and CeO_2). The review is based on a total of 11 modelling studies and 11 analytical studies published between 2008 and 2013. It is noted by Gottschalk et al. (2013) that not all of the analytical measurements represent only the "true" nano-fraction, i.e. only particles <100 nm, but in some cases include particles up to 450 nm corresponding to the pore size of a standard laboratory filter (0.45 µm). The comparison of results is hampered by the different geographies, scales and scopes of the studies and of the different analytical methodologies applied (in particular those only allowing determination as size <450 nm (which includes the dissolved fraction)).

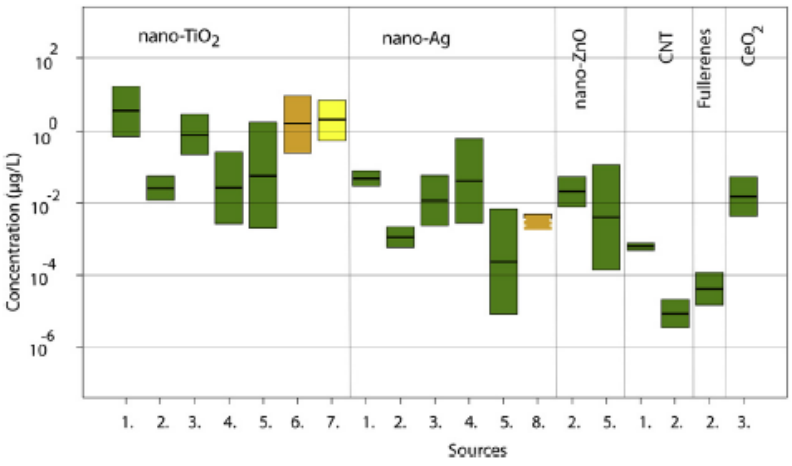


FIGURE 4-1 MODELLED AND ANALYTICAL CONCENTRATIONS OF ENMS IN SURFACE WATERS (FROM GOTTSCHALK ET AL., 2013).
GREEN BOXES ARE MODELLED RESULTS, YELLOW BOXES ARE MEASURED RESULTS AND ORGANGE BOXES ARE COMBINED MODELLED-MEASURED RESULTS.

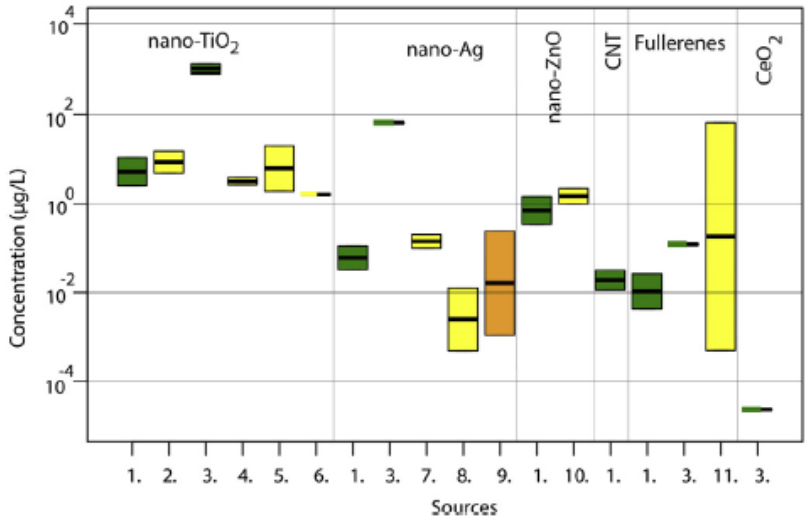


FIGURE 4-2 MODELLED AND ANALYTICAL CONCENTRATIONS OF ENMS IN WASTE WATER TREATMENT PLANT EFFLUENTS (FROM GOTTSCHALK ET AL., 2013).
GREEN BOXES ARE MODELLED RESULTS, YELLOW BOXES ARE MEASURED RESULTS AND ORGANGE BOXES ARE COMBINED MODELLED-MEASURED RESULTS.

4.2.1.2 Groundwater

No results, neither measured nor modelled, have been identified for nanoparticles in groundwater (an important source of drinking water, not at least in Denmark).

4.2.1.3 Tap water/water works water

Tiede et al. (2011) prepared a review for DEFRA (UK) on the risks posed to drinking water by man-made nanoparticles. They concluded that for the majority of the product types assessed, the exposure via drinking water was less important than exposure via other routes. For a few product types and ENMs, the exposure via drinking water was, albeit very low, more significant than from other routes. The product types were some clothing materials, paints and coatings and cleaning products, and the ENMs included Ag, Al/Al_2O_3, TiO_2, Fe_2O_3 and carbon based materials.

As shown below, the predictions were based on surface water as the source of the drinking water (assuming 97% removal of particles in the WWTP process) and considered three treatment scenarios at the water works/water treatment plants, namely conventional treatment (coagulation, flocculation), membrane filtration and direct (ultra)filtration. Membrane filtration seems to lead to the lowest degree of exposure, about three orders of magnitude lower than in the raw water received at the water works.

TABLE 4-2 ENP MASS CONCENTRATION ESTIMATES FOR WTP INFLUENT AND EFFLUENTS – ASSUMING 97% PARTICLE REMOVAL IN WWTP AFTER O'MELIA (1980)

Type	Removal WWTP	WTP (influent) ug/L	WTP (conventional) ug/L	WTP (membrane) ug/L	WTP (filtration) ug/L
Titanium oxide	97%	4.91E+00	4.91E+02	4.91E+04	1.55E-01

Type	Removal WWTP	WTP (influent) ug/L	WTP (conventional) ug/L	WTP (membrane) ug/L	WTP (filtration) ug/L
Zinc oxide	97%	1.91E+00	1.91E+02	1.91E+04	6.03E-02
Silica	97%	1.20E+00	1.20E+02	1.20E+04	3.79E-02
Ceramic	97%	1.10E+00	1.10E+02	1.10E+04	3.48E-02
Carbon & C60	97%	6.62E-01	6.62E-03	6.62E-05	2.09E-02
Carbon	97%	6.60E-01	6.60E-03	6.60E-05	2.09E-02
Iron oxide	97%	6.60E-01	6.60E-03	6.60E-05	2.09E-02
Silver	97%	3.21E-01	3.21E-03	3.21E-05	1.02E-02
Keratin	97%	2.48E-01	2.48E-03	2.48E-05	7.84E-03
Ca peroxide	97%	2.15E-01	2.15E-03	2.15E-05	6.80E-03
Encapsulates	97%	5.92E-02	5.92E-04	5.92E-06	1.87E-03
Aluminium & aluminium oxide	97%	3.87E-03	3.87E-05	3.87E-07	1.22E-04
Silazane	97%	3.00E-03	3.00E-05	3.00E-07	9.49E-05
C60	97%	1.73E-03	1.73E-05	1.73E-07	5.47E-05
Cerium oxide	97%	1.40E-06	1.40E-08	1.40E-10	4.43E-08

Further, some nano-products were identified, which specifically are designed to be used for treatment of drinking water, e.g. nano-silver to be applied at a concentration of 60 ppb for drinking water purposes (www.nanobiosilver.com). Also zero-valent nano-iron (NZVI) is said to be marketed for this use, although the main use is for groundwater contamination remediation. Tønning et al. (2014) mention that also titanium dioxide-based nano-products for drinking water treatment exist.

4.2.1.4 Overall evaluation of the data

Overall, it can be concluded that very few data on measurements of NPs in drinking water (including surface water as a possible raw material for drinking water) are available. The few measurements available are not able to distinguish between engineered nanoparticles (ENPs) and naturally occurring NPs.

This is due partly to severe analytical constraints at present, and partly to the fact that NPs are influenced by a large number of transformation processes (e.g. agglomeration and aggregation), when they enter the environment, which change the original characteristics of the particles.

Hence, most of the estimates of NP concentrations in water that exist are model-based, associated with high uncertainty and may vary orders of magnitude for a specific nano-material.

4.2.2 Possible sources of NMs in drinking water

In general, NMs will presumably only occur in drinking water at relevant concentrations if the source of the raw water is surface water, which is likely to have received NPs with effluents from wastewater treatment plants.

The most likely sources to NMs in this liquid waste stream are an increasing range of consumer products including cosmetics, personal care products, cleaning agents and paints and other coatings. Locally, specific industrial sources may be significant. Thus Keller et al. (2014) estimate that in the USA zinc oxide and titanium dioxide represent 94% of the NPs from personal care products ending up in the environment (including landfills) of which 28-32% enter water bodies.

Some nano-products based on e.g. nano-Ag and nZVI exist that are designed for treatment of drinking water (see section 4.2.1.3). However, no results of measurements of the possible content of residues of these products in the treated drinking water have been identified.

4.3 Soil

Practically no measured data on NPs in soil are available because of huge analytical problems due to the complex matrix with a high degree of interference from other (natural) particles.

Some model-based estimates of soil concentrations of a number of NPs are provided in Section 4.2.1.1. The underlying studies are described briefly in the same section.

4.3.1 Measurement of nanoparticles/ ultrafine particles

4.3.1.1 Agricultural soil

Gottschalk et al. (2013) provide in their review of measured and modelled environmental concentrations of engineered nanomaterials (ENMs) a comparison of various modelled results for the soil compartment showing that even with sewage sludge application, the resulting soil concentrations will mostly not reach the µg/kg level. See Figure 4-3 below.

However, the results for soils do show that sludge application (study no. 2 marked with red dots) will increase the ENM concentration in the soil with almost two orders of magnitude compared to soils that only receive ENMs via the atmospheric compartment (deposition) or direct ENMs product application.

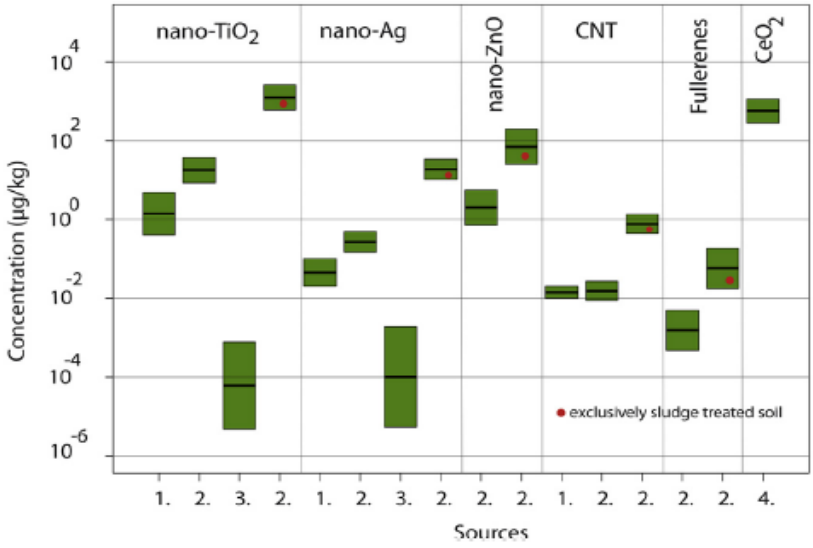


FIGURE 4-3 MODELLED CONCENTRATIONS OF ENMS IN SOILS AND SOILS TREATED WITH BIOSOLIDS (FROM GOTTSCHALK ET AL., 2013). GREEN BOXES ARE MODELLED RESULTS, YELLOW BOXES ARE MEASURED RESULTS AND ORGANGE BOXES ARE COMBINED MODELLED-MEASURED RESULTS.

4.3.1.2 Urban soil

No data have been identified.

4.3.1.3 Contaminated, industrial sites

No modelled or measured data have been identified but nano-zero-valent iron (NZVI) is used in some cases to remediate contaminated groundwater resources because of its ability to transform a range of halogenated groundwater contaminants into less toxic compounds by dechlorination (in particular under reductive conditions). The concentrations used are typically in the range 1-10 g/L (as a slurry), (Mueller et al., 2012).

4.3.2 Possible sources of NMs in soil

With regard to the entry of nanoparticles to the soil environment from general deposition from the atmosphere, reference is made to Section 2.2.2 where sources to nanoparticles in the air compartment are described.

Application of sewage sludge to (agricultural) soil is considered to be the main direct source of nanomaterials to the soil environment (see e.g. Figure 4-3) (Gottschalk et al., 2013)).

Sun et al. (2014) provide the following estimates of ENMs in urban sewage sludge from STPs (EU regional scenario, the estimates for Switzerland are approximately twice as high), see Table 4-3. The estimates are based on probabilistic modelling applying data on the total consumption of a number of ENMs in a defined region (here the EU) and distribution of their mass to different product categories. The product life-cycles then determine any possible releases into the environment.

TABLE 4-3 ESTIMATED LEVELS (MODE = MOST PROBABLE AND 15% AND 85% PERCENTILES; $Q_{0.15}$ AND $Q_{0.85}$, RESPECTIVELY) OF SELECTED NANOMATERIALS IN URBAN SEWAGE SLUDGE AT REGIONAL LEVEL IN THE EU BASED ON PROBABILISTIC MODELLING (SUN ET AL., 2014)

NM	Mode (mg/kg)	$Q_{0.15}$ (mg/kg)	$Q_{0.85}$ (mg/kg)
Ag	0.02	0.01	0.08
CNT	0.15	0.12	0.23
Fullerenes	0.09	0.05	0.22
TiO_2	170	150	540
ZnO	24	17	110

Sewage sludge is typically applied to soil in amounts of some tons per hectare per year. In Denmark, there are limitations on the amounts that can be applied. The limits are (according to the "Statutory Order on sludge"[1]) max. 7 tons sludge dw/ha/year on agricultural land as an average over 10 years and max. 15 tons/ha/year in forests and parks, also calculated as an average over 10 years.

Other possible, direct sources of NMs in the (agricultural) soil environment could include additives to plant protection products (pesticides), inorganic, solid fertilizers (unintended content, produced by tear and wear of the granules) and exhaust from tractors and other machinery (typically with diesel engines) operating in the fields during ploughing, sowing, fertilizing, pesticide spraying and

[1]) Miljøministeriet (2006). Bekendtgørelse nr. 1650 af 13.12.2006 om anvendelse af affald til jordbrugsformål (Slambekendtgørelsen). (Statutory Order on the use of waste for agricultural and related purposes).

harvesting. However, this is only speculative as no description/documentation in relation to nanomaterials has been identified.

4.4 Exposure and risk

Due to the very limited number of data on NPs in drinking water and soil and the large variability and uncertainty associated with the data (mostly model based) available, it is not presently considered meaningful to develop exposure scenarios for risk assessment of human exposure to NPs from soil and drinking water.

5. Exposure to ultrafine particles from the environment, perspective

5.1 Exposure overview

From the data presented in Chapter 2, 3 and 4 an overall view can be made on the everyday exposure to nanoparticles from the environment. As indicated in the Chapters 2 and 3 data on ultrafine particles in ambient air and indoor air allow for estimations regarding the daily population exposure to ultrafine particles, whereas data in relation to exposure from soil and drinking water are too sparse in order to provide any meaningful estimates.

As exposure to ultrafine particle can only be estimated from the particle content in ambient air and indoor air the only exposure route that can be considered from environmental exposure is the inhalational exposure route.

5.1.1 Ambient air

In Denmark average (annual) ultrafine particle levels in the range of **4 000-15 000 particles/cm^3** have been found from measurement in rural background and busy urban areas. During a day at specific hot spot locations with heavy traffic peak levels up to 180 000 particles/cm^3 have been reported.

Thus average daily exposure from 24 hours exposure to outdoor ultrafine particles would for an **adult person** with a daily ventilation volume of 20 m^3 result in daily exposure of:

4000-15 000 particles/cm^3 x 20 m^3 x 10^6 (cm^3/m^3) = **8-30 x 10^{10} particles per day**
or for a person weighing 70 kg exposure would be **1-4 x 10^9 particles/kg/day.**

For **small children** the exposure is higher as their inhalation rate is higher compared to adult. Thus children (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to:
4000-15 000 particles/cm^3 x 0.5 m^3/kg/day x 10^6 (cm^3/m^3) = **2 – 7.5 x 10^9 particles/kg/day.**

It has however to be noted that such exposure figures only gives indication of the exposure level to free ultrafine particles, and that a large fraction of particles above 100 nm in the PM2.5 fraction is due to agglomerated ultrafine particles primarily from the combustion related sources. In urban area about 1/3 of the average PM2.5 level at about 18-20 µg/m^3 is due to these combustion related fractions. Therefore, it can be assumed that about 30% of the overall PM2.5 exposure may be due to free but mostly agglomerated ultrafine particles.
This would correspond to an average exposure to ultrafine particles or agglomerates thereof of about of about **5-6 µg/m^3**.

Assuming a daily ventilation rate of 20 m^3 for an adult person in urban environment this would lead to a daily exposure to **100-120 µg/day of** free plus agglomerated ultrafine particles. For a person

of 70 kg a daily inhalational dose of up to **1.4- 1.7 µg /kg bodyweight/day** may be assumed for free plus agglomerated ultrafine ambient air particles.

Children (1-5 years old) inhaling 0.5 m^3/kg/d would be exposed to:
5-6 µg/m^3 x 0.5 m^3/kg/day = **2.5-3 µg /kg bodyweight/day.**

5.1.2 Indoor air

Great variations in daily indoor exposure to ultrafine particles can be seen from the data by Bekö et al. (2013) that measured indoor levels of ultrafine particles continuously for 45 hours in 56 Danish homes in the period from October to February. The average particle number concentration during a day (24 hours) ranged from 1.5 x 10^3 ultrafine particles/cm^3 in one home to 2.5 x 10^5 ultrafine particles/cm^3 in another home, i.e. a difference of a factor of 100 (97% of the high exposure was from the use of candle lights).

An overall mean 24 hour exposure level 15 600 particles/cm^3 was calculated and a mean integrated exposure level of 334 000 particles (hour/cm^3/day) was found from all the measurement in the 56 homes.

Thus, for **an adult person** inhaling 20 m^3 per day, this would result in a daily inhalation of:
334 000 particles (hour/cm^3 /day) x 20m^3/24 hour /day x 10^6 (cm^3/m^3) = **2.8 x 10^{11} particles/day** or about **4 x 10^9 particles/kg bw day** for a person weighing 70 kg.

Small children (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to:
334,000 particles (hour/cm^3 day)/24 hour /day x 0.5 m^3/kg/day x 10^6 (cm^3/m^3) = **7 x 10^9 particles/kg/day.**

On average 30% of the particle levels was considered as background levels whereas the remaining part of about 70% was considered due to additional sources/activities in the home.

The composition of the various fractions of the ultrafine particle exposure may vary a lot depending of the source. However, very little has been found on measurements of the chemical content of the ultrafine particles.

With respect to mass based exposure estimate to ultrafine particles + agglomerates thereof this estimate may be based on typical indoor PM2.5 levels of 20-30 µg/m3 as indicated from German data, as the presented Danish data are from flats with aged people and therefore considered to be less representative for an average population exposure.

If it is assumed – as for the ambient air particles- that 1/3 of the indoor PM2.5 level stems from ultrafine + agglomerated ultrafine particles this would correspond to an exposure level of **7-10 µg/m^3**.

If **an adult person** daily inhales 20 m^3 air, this would result in a daily exposure of **140-200 µg/m^3 of ultrafine particles**. With a bodyweight of 70 kg this would correspond to **2-3 µg/kg/ day**.

Small children (1-5 years old) inhaling 0.5 m^3/kg/day would be exposed to 7-10 µg/m^3 x 0.5 m^3/kg/day = **3.5-5 µg/kg/day.**

5.1.3 Personal exposure during a day

As indicated by the figure below where data from person borne measurements of ultrafine particle levels during a day is given the personal exposure to ultrafine particles very much depend of the daily activities of the person.

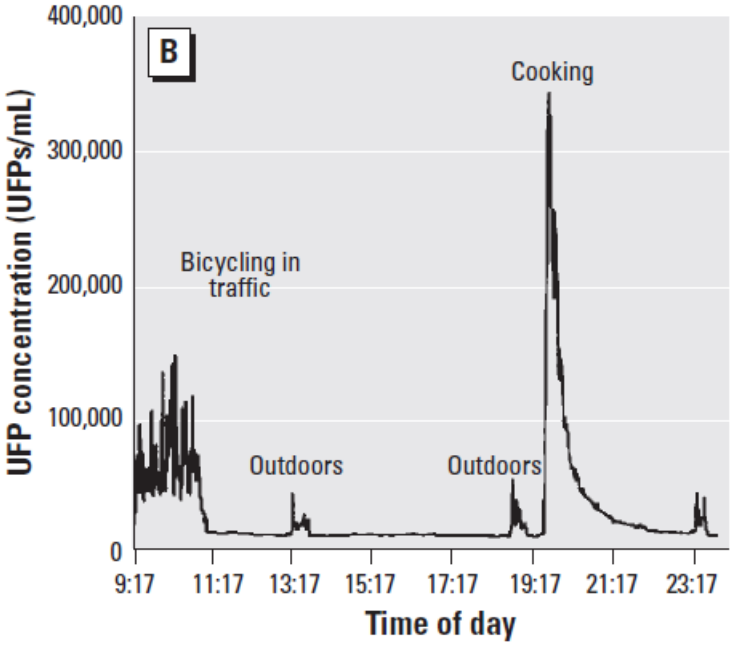


FIGURE 5-1 TIME SERIES MEASUREMENT OF ULTRAFINE PARTICLES ON A TEST DAY WHEN BIKING IN TRAFFIC DURING RUSH HOUR IN COPENHAGEN (DANISH EPA 2005; VINZENTS ET AL., 2005))

Therefor the best method for having a measure for the daily and average exposure is to ultrafine particles would be data from person borne measurement for 24 hours during various periods that will represent a whole year and activity pattern of a person. Here there would be great individual variability for different subgroups in the population depending of:

- Time spend outdoors in various out door environments
- Time spend indoors in various indoor environments
- Duration of various activities of the person
- The ventilation rate of the person

However when looking at the estimates for average **outdoor (4 000-15 000 particles/cm^3)** and **indoor (15 600 particles/cm^3)** exposure levels of ultrafine particles the indoor exposure to free ultrafine particles will over a day dominate due to both a higher exposure levels and a greater fraction of the time spent indoors compared to outdoors.

Also in relation to the mass based exposure levels to ultrafine particles (free plus agglomerated) the estimated exposure level **indoor of 7-10 µg/m^3** exceed the estimated exposure levels **outdoor of 5-6 µg/m^3.**

5.1.4 Exposure to nanomaterial from consumer products

In another part of this project the exposure to nanomaterials from the use of selected consumer products have been estimated. Both exposure estimates in relation to oral, dermal, inhalational and eye exposure were made whatever considered most relevant for the specific product.

When assessing exposure to nanoparticles from environment and from consumer products comparison can only be made for the inhalational exposure route, as no estimates on oral and dermal exposure from environmental media has been made.

In the other part of the project the following inhalational exposure estimates have been considered relevant for the following six products:

1 Use of **face powder** product containing 10 w/w% of nano-silica.
When using applying this product by brush once daily the following nanoparticle exposure was estimated to:
0.26 mg/m^3 in the inhaled air for an application period of 15 minutes corresponding to
0.051 mg/day, or
0.0009 mg/kg/day
and
10 000 particles (20 nm)/cm^3 corresponding to
2 x 10^9 particles (20 nm)/day

2 Sanding of a surface treated with a layer of 100% nano-TiO2:
18 mg/m^3 in the inhaled air for a duration of 0.5 hours corresponding to
0.22 mg/kg/day

3 Spray painting for 30 minutes with paint containing 1% of nano-Ag:
109 mg/m^3 corresponding to
1.3 mg/kg/day (at the day of application, however a consumer may not apply this paint more than once a year)

4 Surface coating of nano-silica containing (1%) propellant spray for a duration of 30 minutes
0.0021 mg/m^3 corresponding to
0.000023 mg/kg/day (at the day of application, however the product is only considered used twice a year)

5 Desinfectant *pump* spray containing 1% nano-Ag, used in e.g. bathrooms 10 minutes once a week:
0.0043 mg/m^3 corresponding to
0.000017 mg/kg/day at the day of application
and
(3.4 – 6) x 10^3 ultrafine particles/cm^3

6 Cement containing 5% nano-TiO2. Scenarios with handling and grinding:
Handling:
0.25 mg/m^3 corresponding to
0.042 mg/kg/day
Grinding:
0.75 mg/m^3
0.13mg/kg/day

It should be emphasised that these estimates of nano-particle exposure are based on the nanoparticle content in the product and it may be very uncertain (especially for the paint scenarios with spraying and sanding) to which extent the nanoparticle bound into a liquid or dried paint-matrix actually still can be considered as a nanomaterial.

5.2 Comparison of exposure

A direct comparison between the exposure levels and exposure estimates that have been made may be difficult due to different methods and conditions for the measurements (e.g. different time scales). However, a cautious attempt for evaluating the exposure impact of the various sources and locations can be made from a compilation of the exposure estimates in the following table:

Exposure levels of ultrafine particles			
Environmental exposure levels			
	Particle no/cm³	**mg/m³**	**µg/kg/day**
Ambient air, annual average	4 x 10^3 - 15 x 10^3	0.005 - 0.006	1.4 - 1.7
Indoor air Range 24-hours Average 24-hours	 1.5 x 10^3 – 2.5 x 10^5 14 x 10^3	 0.007 - 0.010	 2 - 3
Personal average 24-hours non-smookers	 9.2-29 x 10^3	 -	 -
Use of products estimated exposure level			
1. Face powder 15 min	>10 x 10^3	0.26	0.9
2. Paint sanding 30 min	-	18	220
3. Paint spraying 30 min	-	109	1300
4. Surface coating 30 min	-	0.0021	0.02
5. Pump spray 10 min	(3.4 – 6) x 10^3	0.0043	0.017
6. Cement Handling 8 hours Grinding 8 hours	 - -	 0.25 0.75	 42 130
Indoor sources, exposure levels			
Frying meat	15 x 10^4	-	-
Electric stove	11 x 10^4	-	-
Gas stove	8 x 10^4	-	-
Radiator	22 x 10^4		
Vacuum cleaning	(2.1-3.8) x 10^4	-	-
Candle burning	(7 – 24) x 10^4	-	-
Cigarette	21 x 10^4	-	-

Particle number concentrations (particle no/cm³)
In the table only a selection of indoor sources is presented. However, the very high number concentrations that have been measured for various indoor sources support that the 24-hours measurements in indoor environment are very much impacted of these sources. Also the personal borne measurements data indicate that the highest daily number based exposure to ultrafine particles comes from the indoor environment and the indoor sources.
Data on particle number concentrations from use of consumer nano-products are sparse. The present data in relation to face powder and pump spray indicate however considerable lower exposure levels compared to many other indoor sources. Furthermore the exposure to the particle number concentration from face powder is very short (less than 15 minutes per day). This may also apply to other consumer product e.g. sprays that are often used only a couple of minutes.

Mass based concentrations (mg/m³ and µg/kg/day)
Very few PM0.1 measurements are available for evaluating the mass based exposure to free ultrafine particles in the air. Thus the mass based concentrations estimated here include the exposure estimate for both free and agglomerated ultrafine particles.

In relation to the exposure levels from the products these have been made based on the fraction of nano-material used in the product. It is, however, – especially for the spray paint and sanding paint scenarios due to the binding of the nanomaterial in a liquid or dried matrix – very uncertain to which extent this exposure actually reflect exposure to nanomaterials.

For other product scenarios such as face powder and cement considerable higher mass based concentrations may be reached compared to ambient and indoor levels. It should be noticed that the average daily exposure (expressed in µg/kg/day) for face powder is nearly at the level of the environmental exposure, whereas the daily exposure from cement is considerably higher.

The estimated exposure level to nanomaterials of 0.004 mg/m^3 from pump spray containing 1% of nanomaterial is not considered to exceed the environmental levels of ultrafine particles. Thus the daily exposure from a pump spray used in 10 minutes is in this case estimated to result in a daily exposure 2 orders of magnitudes lower than the environmental exposures (expressed in µg/kg/day).

5.3 Comparison of risk

Ambient air

As indicated in Section 2.4 and 2.5 series of adverse health effects have been attributed to the content of ultrafine particles (free plus agglomerated particles) in the ambient air especially in relation to long term exposure where increased mortality is the most prominent finding. From the data on PM2.5 in ambient air it may be assumed that 1 µg/m^3 ultrafine particles (free plus agglomerated particles) as an annual exposure level is associated with an increase in mortality of at least 0.6%. This may be put into perspective as the current annual levels of free plus agglomerated ultrafine particles in in Denmark is assumed to be in the range of 5-6 µg/m^3 .

Indoor Air

Due to many indoor emission sources of ultrafine particles the levels of free ultrafine particles as well as the levels of free plus agglomerated ultrafine particles are considered higher than the ambient exposure.

However, data on the human health hazards in relation to indoor particle levels is very poor and at present often the same dose-response relationship as for the ambient air particles is used. However, it should be emphasised that great uncertainties applies to this approach.

Consumer nano-product

Even less data than for indoor particles are available in relation to the humane health hazard from the nanomaterial exposure from the use of nano-products.

But even though data on ultrafine particle in ambient air call for concern in relation to exposure from manufactured nanomaterials/nanoparticles, it cannot be recommended to extrapolate risk from data on ambient air particles as the composition of the particles from nano-consumer products is quite different from the ambient air particles. Thus, the use of such an approach would be based on pure guesswork rather than substantiated by sound scientific argumentation.

In conclusion and in relation to nanomaterial exposure from consumer product, the most appropriate approach at present time for risk assessment is a case–by-case approach and using data on actual exposure levels and hazard data on the specific nanomaterials. Although both exposure data and hazard data to a great extent are lacking for many nanomaterials, increased research efforts within the latest decade now begin to provide new information and a better understanding of nano-specific properties, so that the basis for more detailed risk assessments is growing and will further grow in the coming years.

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Exposure to nanomaterials from the Danish Environment

Under the Agreement "Better Control of Nanomaterials" (“Bedre styr på nanomaterialer”), the Danish EPA has commissioned a number of projects aiming to investigate and generate new knowledge on the presence of nanomaterials in products on the Danish market and assess the possible associated risks to consumers and the environment.

This report is part of a series of four from a project which addresses consumer exposure and risk assessment of nanomaterials in products on the Danish market. The report evaluates the population’s exposure to nanoparticles from the environment i.e. ambient air, indoor air, soil and water (drinking water) and describes the risk associated with this exposure. The results should give proportionality to the possible risks from exposure to nanomaterials from use of consumer nano-products which are described in other parts/ work packages of this project.

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