Ultrafine Particles

An Update - What, Where, Why, Concern

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Introduction

Personal exposure to ultrafine particles (UFP) occurs every day while people are outdoors or in their homes, offices, and other indoor environments. Sources of indoor UFP are numerous and typically result from particular activities, such as cooking, cleaning, smoking tobacco products, or operating consumer appliances or some types of commercial imaging devices. Even though there is a plethora of outdoor UFP sources, including vehicle emissions and outdoor air pollution, studies suggest that indoor sources are greater than outdoor sources for a typical non-smoking suburban consumer (Wallace and Ott 2011).

Ultrafine particles are very small, typically less than $0.1~\mu m$ or less than 100~n nanometers (or about $1/1000^{th}$ of a human hair). By virtue of their size, they can be easily inhaled and travel deep into the human lung. Results of studies to date have indicated a strong correlation between UFP exposure and death from respiratory and cardiovascular illnesses, as well as a heightened allergic inflammation that can exacerbate asthma. The US Environment Agency (US EPA) reports that researchers estimate that thousands of elderly people die prematurely each year from exposure to fine particles. According to the American Academy of Pediatrics, children and infants are also very susceptible to health problems from exposure to many air pollutants (US EPA 2011a).

The following provides an overview of UFP and indoor air quality (IAQ).

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Particle sizes

Airborne particles sizes are expressed as microns (μ m) or nanometers (nm) in diameter (1 μ m equals 1000 nm or 1 nm equals 0.001 μ m). Particles can range in size from very small (0.001 μ m to 10 μ m), that can remain in the air for a long time, up to relatively large (100 μ m), that quickly settle out of the air. Ultrafine particles are generally defined as those that are less than 0.1 μ m (less than 100 nm) in size. Airborne particles can be classified into three modes, according to their diameter and formation mechanisms, each of which may have very different sources and composition (Nazaroff 2004):

- **Nucleation mode.** UFP measure less than 0.1 μm or less than 100 nm. They are formed by nucleation, which is the initial stage in which gas becomes a particle. These particles generally consist of primary combustion products and reactions between gaseous compounds. They can grow in size either through condensation (when additional vapors condense on the particles.) or through coagulation (when two or more particles combine to form larger particles).
- **Accumulation-mode.** Particles receive this designation when they grow to a size of between 0.1 μm and 2.5 μm in diameter. They originate from primary emissions, chemical reactions, condensation, and coagulation.
- Coarse-mode particles. These particles measure greater than 2.5 µm in diameter, and they are most frequently generated by mechanical processes.

An often used simple classification for particles uses two basic modes: **fine** (\leq 2.5 µm) and **coarse** (> 2.5 µm), with UFP a subset of the fine particles.

Ultrafine particles can be also referred to as nanoparticles, which include all engineered and ambient nanosized, spherical particles. Other engineered nanosized structures are labeled according to their shape, such as nanotubes, nanofibers, and nanowires.

To give some perspective about the size of UFP, deoxyribonucleic acid (DNA) is 2.5 nanometers (0.0025 μ m) in diameter; a typical protein, such as hemoglobin, is 5 nanometers (0.005 μ m) in diameter; and a sheet of paper is about 100,000 nanometers (100 μ m) thick. Table 1 lists some common indoor contaminants and their particle sizes.

Table 1. Particle size of common indoor air contaminants*

| Particle | Size (μm) | Particle | Size (μm) |
|---------------------|---------------|---|-----------|
| Skin flakes | 1-40 | Asbestos | 0.25 – 1 |
| Visible dust, lint | > 25 | Re-suspended dust | 5 – 25 |
| Dust mite | 50 | Environmental tobacco smoke | 0.1 – 0.8 |
| Mite allergen | 5 – 10 | Diesel soot | 0.01 – 1 |
| Mold, pollen spores | 2 – 200 | Outdoor fine particles (sulfates, metals) | 0.1 – 2.5 |
| Cat dander | 1-3 | Fresh combustion particles | < 0.1 |
| Bacteria+ | 0.05 – 0.7 | Metal fumes | < 0.1 |
| Viruses+ | < 0.01 – 0.05 | Ozone- and terpene-formed aerosols | < 0.1 |
| Amoeba | 8 – 20 | Mineral fibers | 3 – 10 |

^{*} McDonald and Ouyang 2000.

Particle measurements

Airborne particles are measured and typically reported in two units. One is number concentration, which is the total number of airborne particles per unit volume of air, without distinction as to their sizes. This is reported as number of particles per unit of air or particles/cm³ or particles /m³. The other is mass concentration, which is the total mass of all particles in an aerosol per unit volume of air. Mass concentration is reported as nanogram (ng) or microgram (µg,) of particles per volume of air as $\mu g/m^3$, ng/m^3 , $\mu g/cm^3$ or ng/m^3 . Since UFPs reach high number concentrations, but their mass is very small, these sub-micron particles are typically expressed in particle number concentrations or particles/cm³.

Particle Standards

EPA under the Clean Air Act established National Ambient Air Quality Standards (NAAQS) for certain criteria pollutants including particles. There are two types of national air quality

⁺Occur in larger droplet nuclei.

standards for particles including: **Primary Standards** that set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly and **Secondary Standards** protect public welfare, including protection against visibility impairment, damage to animals, crops, vegetation, and buildings.

The U.S. air quality standards for particles were first established in 1971 and were not significantly revised until 1987, when EPA changed the indicator of the standards to regulate inhalable particles smaller than, or equal to, 10 microns in diameter, known as PM_{10} . Ten years later, EPA revised the standards, setting separate standards for fine particles smaller than, or equal to, 2.5 microns in diameter, known as $PM_{2.5}$. The fine particle standard was based on their link to serious health problems ranging from increased symptoms, hospital admissions and emergency room visits for people with heart and lung disease, to premature death in people with heart or lung disease.

Current outdoor air quality standards are given below in Table 2. Since there are no regulated standards for the indoor air, these 24 hour standard values for outdoor air are often used as default criteria for indoor air. EPA recognizes ultrafine PM as an emerging issue where more research on health effects and controls are needed.

Table 2. National US Ambient Air Quality Standards for Particles

| Pollutant | Primary Stds. | Averaging Times | Secondary Stds. |
|---|------------------------|--|------------------------|
| Particulate Matter (PM ₁₀) | Revoked ⁽¹⁾ | Annual ⁽¹⁾ (Arithmetic Mean) | |
| | 150 μg/m ³ | 24-hour ⁽²⁾ | Same as Primary |
| Particulate Matter (PM _{2.5}) | 12.0 μg/m ³ | Annual ⁽³⁾ (Arithmetic Mean) | 15.0 μg/m ³ |
| | 35 μg/m ³ | 24-hour ⁽⁴⁾ | Same as Primary |

(see the complete table of National Ambient Air Quality Standards at http://www.epa.gov/air/criteria.html) Units of measure for the standards are micrograms per cubic meter of air (µg/m³). Footnotes:

Human Health Risks

Health risks from exposure to particles follow a basic principle. The smaller the particle, the greater the risk. As the size of a particle decreases, its surface area increases, which allow a greater proportion of its atoms or molecules to be displayed on the surface rather than the interior of the material (see Table 3). This larger surface area permits these particles to carry

^{(1) -} Due to a lack of evidence linking health problems to long-term exposure to coarse particle pollution, the agency revoked the annual PM_{10} standard in 2006 (effective December 17, 2006).

^{(2) -} Not to be exceeded more than once per year on average over 3 years.

^{(3) -} To attain this standard, the 3-year average of the weighted annual mean PM_{2.5} concentrations from single or multiple community oriented monitors must not exceed 12.0 µg/m³.

^{(4) -} To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 μ g/m³ (effective December 17, 2006).

greater amounts of toxins. UFP make up the majority of ambient particles and a significant portion of the total surface area of all the airborne particles in a given sample (Nel et al 2006, Bernstein et al 2008, and Morawska et al 2006, Nazaroff 2004).

Table 3. Particle number and particle surface area for 10 mg/m³ airborne particles (5).*

| Particle Diameter (μm) | Particles / ml air | Particle surface area (μm² / ml air) |
|------------------------|--------------------|---|
| 2.5 | 1.2 | 24 |
| 2 | 2 | 30 |
| 1 | 19 | 60 |
| 0.5 | 153 | 120 |
| 0.1 | 19,100 | 600 |
| 0.02 | 2,40,000 | 3,016 |

^{*}Nel et al 2006, Oberdörster 1995 as reported in Keady and Manquist 2000

Respiratory and cardiovascular effects

In a comprehensive report, "Determination of the State of Health Science for Ultrafine Particles", researchers conclude that the array of epidemiological studies suggest that UFP exposure is associated with adverse respiratory and cardiovascular effects. The limited number of epidemiological studies suggests that there are comparable health effects of fine and ultrafine particles, but that fine particles show more immediate effects while UFP show more delayed effects on mortality (Morawska et al 2006).

Acute effects from the number of UFP on respiratory health are stronger than the mass of the UFP. In addition, effects of UFP exposure on adults with asthma appear to be more severe than for children with asthma. Effects due to inflammation in the lungs do not occur immediately but develop over hours and days. Cumulative effects over five days appear to be stronger than same-day effects. Researchers cautioned that more research is needed to generalize these results (Morawska et al 2004).

Health care professionals are especially concerned about the long-term effects of inhaling UFP because they can travel deep into the tracheobronchial region and alveoli regions of the lungs where they can remain embedded for years or be absorbed into the bloodstream. Exposure to high levels of UFP also can cause oxidative stress and inflammation in the lungs. This leads to the development of and exacerbation of respiratory diseases such as asthma, pneumonia, and chronic obstructive lung disease (COPD), which includes chronic bronchitis and emphysema. Larger particles (> $10~\mu m$) do not cause as much concern, because they get caught in the nose and throat and are cleared from the respiratory tract by coughing or swallowing (ALA Special Report on Air Cleaners, Bernstein et al 2008, Weichenthal et al 2006).

With respect to cardiac health, one hypothesis is that UFP deposited in the alveoli lead to increased blood clotting, as a result of either pulmonary inflammation or a direct action of inhaled UFP on red blood cells. An alternative hypothesis is that the cardiovascular effects are caused by an alteration of the autonomic control of the heart. This theory is supported by epidemiologic studies on heart rate, heart rate variability, and arrhythmia (de Hartog et al 2003).

Childhood asthma

Several studies have investigated how UFP influence the development of childhood asthma. The onset of asthma typically involves a shift in the balance of immune function from a cell-mediated immune response involving T-helper type 1 lymphocytes (Th1) to an antibody-mediated immune response involving T-helper type 2 (Th2) lymphocytes. In general, this shift involves developing an immunological memory to inhaled allergens through the production of specific immunoglobulin (IgE) antibodies. As a result, people who are repeatedly exposed to allergens become prone to airway distress. Exposures to UFP also might promote or enhance Th2 type immune responses following exposure to biological risk factors for childhood asthma, such as respiratory syncytial virus (RSV). The potential ability of UFP to promote a Th2 type immune response may be one method by which indoor UFP exposures promote this disease. These findings are important, because RSV infections are common among infants. Approximately 90 percent of infants and young children are affected by 2 years of age (Weichenthal et al 2006).

Nanoparticles

Researchers are investigating the potential health effects from exposure to engineered nanosized particles (NSPs), the smallest of ultrafine. The results of various studies have demonstrated that when inhaled, NSPs are efficiently deposited in all regions of the respiratory tract. The small size facilitates uptake into and across epithelial and endothelial cells into the blood and lymph circulation to reach potentially sensitive target sites such as bone marrow, lymph nodes, spleen, and heart. Access to the central nervous system and ganglia along axons and dendrites of neurons has also been observed. Nanosized particles also can penetrate the skin and find their way into the lymph nodes and channels (Oberdörster et al 2005).

How NSPs enter and affect individual cells and their functions largely depends on NSP particle coating, surface treatments and excitation by ultraviolet (UV) radiation, and particle aggregation, all of which can modify the effects of particle size. The greater surface area per mass compared with larger-sized particles of the same chemistry renders NSPs more biologically active. This activity includes a greater potential for inflammatory and pro-oxidant, but also antioxidant, activity. It is possible, therefore, that some nanoparticles may exert toxic effects as aggregates or through the release of toxic chemicals. More research is needed to fully understand these mechanisms. (Oberdörster et al 2005, Nel et al 2006).

UFP Sources and Levels

People have been exposed to airborne particles of varying sizes throughout history. Since the industrial revolution, ambient particle concentrations and exposure have increased dramatically as a result of human-generated (anthropogenic) sources, both intentional and unintentional (see Table 4). Table 5 lists common indoor sources of UFPs, which are discussed in detail below.

Table 4. Natural and anthropogenic sources of particles (Oberdörster et al 2005)

| Natural | Anthropogenic – Unintentional | Anthropogenic – Intentional (NPs) |
|--|---------------------------------------|--|
| Gas-to-particle conversions | Internal combustion engines | Controlled size and shape, designed for functionality |
| Forest fires | Power plants, incinerators | Metals, semiconductors, metal oxides, carbon polymers |
| Volcanoes (hot lava) | Jet engines | Nanospheres, -wires, -needles, - tubes, -shells, -rings, -platelets |
| Biogenic magnetite: magnetotactic bacteria protoctists, mollusks, arthropods, fish, birds, human brain, meteorite | Polymer fumes and other fumes | Untreated, coated (nanotechnology applied to many products: cosmetics, medical, fabrics, electronics, optics, displays, etc) |
| Viruses | Metal fumes (smelting, welding, etc.) | |
| Ferritin (12.5 nm) | Heated surfaces, electric motors | |
| Microparticles (< 100 nm; activated cells) | Frying, broiling, grilling | |

Table 5. Some indoor sources of UFP

| Combustion processes, cooking, wood burning | Cleaning activities, cleaning products and processes, vented clothes dryer |
|---|--|
| Operating small appliances such as hair dryers, electric toasters, air popcorn poppers, electric mixers, curling irons, steam irons, grills | Candle vaporizing oils, candle burning, aerosol applications |
| Hobby activities – wood making, grilling, gluing,3D printing | Smoking, tobacco products |
| Art activities in schools- painting, gluing, and drawing gluing, | Office equipment- printers, faxes, copy machines, |

Levels

In a comprehensive review of the health impact of UFP, prepared for the Australian Government Department of the Environment it was noted that particle number concentrations in outdoor environments is usually a few hundred particles per cm³. In urban environments, background particle number concentration range from a few thousand to about 20,000 particles per cm³. Near roads and tunnels, motor vehicles are the most significant source of UFP, and number

concentrations can be 10 times higher or more than background and can reach or exceed levels of 10^5 particles per cm³. By contrast, PM₁₀ and PM_{2.5} mass concentrations are only about 25 percent to 30 percent higher than background levels. While there may be more UFPs in a given sample, their mass may be less than PM₁₀ and PM_{2.5}. As a result, UFP levels are expressed as particle number rather than mass concentration. People living or working near a major urban road are likely to be exposed to UFP levels well above what is considered normal background levels and elevated PM₁₀ and PM_{2.5} levels, (Morawska et al 2004).

UFP sources in indoor environments comprise a significant proportion of the total UFP exposure, greater than outdoor sources. Among key sources of indoor particle emissions in homes are combustion processes, cooking, wood burning, and smoking tobacco products, candle burning, operating small appliances such as hair dryers, and cleaning activities. (Nazaroff 2004, Keady and Manquist 2000, Wallace and Ott 2011).

Researchers placed portable monitors in homes, cars, and restaurants over a three-year period. The results showed that for typical suburban nonsmoker lifestyles, indoor sources provide about 47 percent and outdoor sources about 36 percent of total daily UFP exposure. In-vehicle exposures added the remainder (17%). The effect of one smoker in the home, however, caused an overwhelming increase in the level of exposure from indoor sources (77% of the total). (Wallace and Ott 2011).

Specifically, the results showed that cooking on gas or electric stoves and electric toaster ovens was a major source of indoor UFP, with peak personal exposures often exceeding 100,000 particles/cm 3 and estimated mean emission rates of 5 x10 12 particles per minute. Other common sources of high UFP exposures were cigarettes, a vented gas clothes dryer, an air popcorn popper, candles, an electric mixer, a hair dryer, a curling iron, and a steam iron. Relatively low indoor UFP emissions were found for a fireplace, several space heaters, and a laser printer (Wallace and Ott 2011).

Driving resulted in moderate exposures averaging about 30,000 particles/cm 3 in each of two cars driven on 17 trips on major highways on the US east and west coasts. Most of the restaurants visited maintained consistently high levels of 50,000 particles/cm 3 to 200,000 particles/cm 3 for the entire length of the meal. The indoor/outdoor UFP size ratios were much lower than for PM $_{10}$ or PM $_{2.5}$, suggesting that outdoor UFP have difficulty penetrating a home. The researchers concluded that the implication is that outdoor concentrations of UFP have only a moderate effect on personal exposures if indoor sources are present (Wallace and Ott 2011).

As a part of a large study of IAQ in residential homes in Brisbane, Australia, researchers measured concentrations of UFP (referred to as sub micrometer particles) and PM2.5 simultaneously for more than 48 hours in the kitchens of 14 houses. The results showed that cooking, frying, grilling, stove use, toasting, making pizza, smoking, candle vaporizing eucalyptus oil, and fan heater use elevated the indoor particle concentrations from 1.5 to more than 27 times over background levels. Concentrations of UFP increased by 3, 30, and 90 times during smoking, grilling, and frying, respectively. One finding of particular note was that even though the same cooking procedure and the same cooking material were used, the emission rate and number average diameter of the particles varied from house to house (He et al 2004).

Another study investigated 12 household appliances, such as toasters, grills, and hair dryers, as sources of UFP, and found that these appliances were strong particle emission sources even when there was no contact with food or clothing. The devices were new and had never been used for their original purpose. Environmental chamber test results revealed that during the operating phase, these devices emitted particles with an average diameter of less than 100 nm, including high quantities of particles measuring 10 nm in diameter. The origin of the particles was attributed to the heated surfaces, and cleaning these surfaces only had a minor influence on the emission strength. The results also showed that the particles were formed from semi-volatile organic compounds (SVOCs), but the SVOCs themselves were not located on the heated surfaces nor released from the appliances as supersaturated vapor. In addition, the presence of additional organic compounds in the surrounding air influenced particle growth. One other significant finding is the UFP did not require oxygen to form (Schripp et al 2011).

Because UFP have been implicated in childhood asthma, exposure to these very small particles in school classrooms also is a major concern. A recent study investigated levels of UFP (<0.1 μ m) as they related to classroom activities in three primary school classrooms over a period of 60 days. Initial results showed that under the normal operating conditions, there were many occasions in all three classrooms where indoor particle concentrations increased significantly compared with outdoor levels. The highest increases resulted from art activities, such as painting, gluing, and drawing. The indoor particle concentrations exceeded outdoor concentrations by approximately one (1) order of magnitude, with particle sizes averaging 20 nm to 50 nm in diameter (Morawska et al 2009).

Cleaning Processes

Significant increases occurred during indoor cleaning activities, when detergents were used. Analysis of four samples randomly selected from about 30 different paints and glues, as well as the detergent used in the school, revealed that d-limonene was one of the main organic compounds in the detergent, but not detected in the samples of the paints and the glue. Results disclosed that this terpene reacted with ozone at outdoor ambient concentrations ranging from 0.06 ppm to 0.08 ppm and formed secondary organic aerosols, which can have an adverse impact on IAQ. The researchers suspected that other liquids also may be potential sources of precursors to secondary organic aerosols, since most primary schools use liquid materials for art classes and all schools use detergents for cleaning (Morawska et al 2009).

Other studies also have shown that certain volatile organic compounds (VOCs) may react with ozone to produce UFP. As noted, d-limonene and other terpene compounds, used in polishes, scented deodorizers, cigarettes, fabrics, and fabric softeners, can readily react with low concentrations of ozone, brought in from the outdoors or produced by ionizing air cleaners. This reaction creates aldehydes and UFP. The results from another study demonstrated that a mopping agent containing terpene generated vast numbers of ultrafine particles in a reaction with ozone. The results also demonstrated that 10 minutes of mopping with this agent influenced indoor particle concentrations for more than 8 hours (Long et al 2000, Sarwar et al 2002, Wechsler and Shields 1999, Wolkoff et al 2000, Apte and Erdmann 2002),).

Researchers at the University of California - Berkeley, and Lawrence Berkeley National Laboratory found that the application of a pine-oil based cleaner produced an average concentration of $10 \,\mu\text{g/m}^3$ to $1,300 \,\mu\text{g/m}^3$ for terpene hydrocarbons and terpene alcohols.

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Exposing these compounds to ozone, both in bench-scale chamber testing and simulated use, produced formaldehyde and hydroxyl radical, which in turn created an array of other indoor chemical reactions, including an aerosol of fine particles like those found in smog and haze, all of which raises the risk of health problems of those exposed (Nazaroff 2006).

Study of a supermarket in Sweden further demonstrates the role terpenes play in the formation of UFP. In this study, researchers found that the source of UFP inside the supermarket was likely due to local emissions of terpenes from washing powders, cleaning products, and air fresheners. They concluded that more data is needed to determine typical UFP levels in supermarkets, but these results emphasize the importance of adequate ventilation in places where products containing terpenes are kept in order to minimize the formation of and exposure to UFP (Wierzbikca et al 2009).

The formation of UFP also can be directly related to how cleaning products are used. A product may have 10 percent VOCs by weight, which may be low enough to classify it as green or environmentally friendly. If that product is packaged as an aerosol, it may atomize the VOC particles during use and increases the potential for exposure. Atomized particles are smaller and lighter, which means they can be inhaled more deeply into the lung, stay suspended longer in the air than larger, heavier particles, and can travel around an indoor environment easier via the heating, ventilating, and air-conditioning (HVAC) system. If this same product is delivered using a trigger sprayer, course mist, stream, or in a bucket, the risk for exposure diminishes as the particles become progressively larger and heavier and will fall to the ground more rapidly than smaller, lighter particles (Ashkin 2005).

Office equipment

Printers and copy machines are potential indoor sources of particles, ozone, VOCs, and SVOCs. Researchers have observed indoor levels of UFP to increase as much as five times from non-working hours to working hours when certain printers are being used. They also observed that these indoor levels were higher than the UFP levels found in outdoor air as a result of automobile engine combustion and exhaust. The researchers pointed out that some printers emit high levels of UFP, while others do not emit any. The type and age of the printer, print mechanisms, paper type, and toner appeared to affect how many UFP are emitted into the air (Shi, Ekberg and Fahlen 2009, He et al 2007, Wang et al 2010).

For example, a study measured UFP emissions produced by each of 62 printers used in an office building. Based on the particle concentrations in the immediate vicinity of the printers, after a short printing job, the printers were divided into four classes: non-emitters, and low, medium, and high emitters. They found that approximately 60 percent of the printers did not emit UFP, while of the 40 percent that did emit particles, 27 percent were high particle emitters. Particle emission characteristics from three different laser printers also were studied in an environmental chamber, which demonstrated that particle emission rates are printer-type specific and are affected by toner coverage and cartridge age (He et al 2007).

Results from another study contradicted the premise that UFP primarily originate from toner. The results showed that modified laser printers operated without toner or paper also emitted UFP. The researchers believe that the high-temperature fuser unit is one source of these emissions. They also found that the release of UFP typically follows the flow path of the cooling air, which may leave the printer casing at various points, such as the paper tray. In addition, the

results raise doubts about the effectiveness of commercial filter systems attached to printers, because the released particles could leave the printer without passing through the filter (Nel et al 2006).

Emissions from process photocopies, laser printers, and computers were studied over an extended period and participated in the development and validation of test protocols of these and other types of electronic equipment. A review of the data showed a wide range of total VOC (TVOC), ozone, and particle emissions from the equipment, with dry process photocopiers having the highest average TVOC and ozone emission rates and laser printers having lower average TVOC and ozone rates. Personal computers were not a source of ozone, but they did emit TVOC and particles. Particle emissions from the laser printers and photocopiers were similar, with personal computers emitting lower levels of particles. Table 6 provides a summary of the emission rate data from these studies (Black et al 2006).

| Table C Cummon | of Emission | Data Data f | or Office Faulinment | (Dlack 2006) |
|------------------|-------------|-------------|----------------------|--------------|
| Table 6. Summary | of Emission | kate pata t | or Office Equipment | (Black 2006) |

| Equipment / Processes | Average Contaminant Emission Rate mg / h (Range of Values) | | | | | | |
|-----------------------|--|----------------------------------|----------------------|--|--|--|--|
| | TVOC | TVOC Total Particles Ozone | | | | | |
| Laser Printers | 26.4 (1.2 – 130) | 0.9 (<0.02 – 5.5) | 0.8 (<0.02 – 6.5) | | | | |
| Dry Process Copiers | 36.4 (4.6 – 108) | 2.5 (<0.7 – 6.2) | 4.2 (1.2 – 6.3) | | | | |
| Personal Computers | 12.2 (0.05 – 24.2) | 0.05 <0.02 2) (<0.027 – 0.12) | | | | | |

3D Printing

The use of 3D printers and additive manufacturing processes presents a human health concern related to the potential release of chemicals and fine particles into the air during operation. This in return can affect the indoor air quality and expose people to unexpected harmful pollutants. The majority of 3D printers function by 1.) Extruding a hot thermoplastic and depositing it in layers in layer to shape a product according to a model or 2.) Depositing various polymers using inkjet type of heads. Other techniques include sheet lamination, photo-polymerization, and powder fusion bonding. In all cases, a range of materials, plastics, polymers, binding and finishing agents, and metals are used, presenting potential health hazards resulting from volatile organic chemicals, aerosols, and particles released during printing. These may become airborne or may deposit on small dust particles that may also be inhaled or ingested. Typical materials include polycarbonate, polystyrene, polyvinyl alcohol (PVA), acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyethylene terephthalate (PET), and nylon. Printing functions have been shown to be sources of particles, including ultrafine particles (UFPs) that are released into the air.

With the rapid adoption of 3D printers, especially in the consumer market where homeowners, children, educators, and small business, employees can be affected. Research data on their chemical and particle emissions is important in assessing the potential for human health risks and ultimately designing engineering controls and material selection for minimizing risks.

Nanomaterials

Nanomaterials are engineered structures that are increasingly being used for commercial purposes such as fillers, catalysts, semiconductors, cosmetics, microelectronics, and drug carriers. Carbon nanotubes (CNTs) have greater mechanical strength and less weight per volume than that of conventional materials. Due to their electronic properties, they also are used in flat

panel displays in televisions, batteries, and other electronics. In addition, CNTs exhibit great potential for enhancing the effectiveness of air filters in removing bioaerosols, such as bacteria, fungi, viruses, endotoxin, glucans, and mycotoxins (Guan and Yao 2010). Another example is nanotransistors, which are used like a gate to control the flow of larger amounts of electricity. In computers, the more transistors, the greater the power. Thus, smaller transistors mean more transistors may be used (National Nanotechnology Initiative).

There is concern that even though nanomaterials show great promise, the nanosized particles that comprise these materials could pose potential health risks, including harmful interactions at the cellular level. In response, researchers in the field of nanotoxicology are working to establish principles and test procedures to ensure safe manufacture and use of nanomaterials in the marketplace (Nel et al 2006, Oberdörster et al 2005).

Control Strategies

Indoor emissions of particles tend to be episodic and localized. Consequently, the effects of emissions on inhalation exposure depends not only on the source but also on infiltration, indoorair mixing, transport, resuspension, coagulation, and environmental conditions. Since ultrafine particles weigh almost nothing, they can stay airborne for a long time and easily move from one area of a building to another based on small pressure differentials between spaces, as well as through unexpected pathways, such as cracks in walls and floors (Keady and Manquist 2000, Nazaroff 2004).

Influencing factors Include:

- Mixing. Indoor airflow may be induced by mechanical means, such as air discharge from ventilation registers, flow through an open window, or people moving within a room. Buoyancy from temperature differences can encourage natural convection flow that contributes to mixing. For example, air will flow upward (downward) along an exterior wall that is warmer (cooler) than the core room air. However, temperature differences can also impede mixing when warmer air is above cooler air. Mixing of the air not only can move particles from one place to another but also affects the time they are suspended in the air.
- Zone transport. Airflow between rooms can strongly influence particles and other
 indoor air pollutant concentrations and how they are eventually dispersed,
 dissipated, or removed. Variables affecting the rates of interzonal flow, such as
 pressure differences caused by drafts, temperature differences, and fan operation,
 are understood in principle, but only a few studies have explored them as they
 relate IAQ.
- Resuspension. Ordinary indoor activities, such as walking and housekeeping, can
 cause particle resuspension and may also generate new particles through abrasive
 wear of surfaces. As with interzonal transport, only a few studies have investigated
 these variables. Other studies have suggested that particle resuspension may be an

important exposure pathway for allergens and semivolatile compounds (SVOCs) such as phthalate esters (Institute of Medicine 2000, Clausen et al 2003).

- Coagulation. UFP can adhere to each other or combine to form larger particles.
 Coagulation does not directly cause a change in particle mass concentration. It does, however, shift particle size distributions, resulting in a transfer of suspended particle mass from the ultrafine mode into the accumulation mode. When concentrations are unusually high, such as in the presence of a fresh source of particle emissions, coagulation becomes more important than at other times.
- Phase-change processes. Indoor particulate matter can be altered via phase-change processes, in which chemicals undergo a change of state from gas phase to condensed phase or vice versa. Examples of phase-change processes that may affect indoor particles include:
 - Changing humidity conditions can influence particle size growth, from the release or uptake of moisture.
 - Phase partitioning of SVOCs between the gas-phase may be absorbed into indoor airborne particles.
 - Production of secondary organic particulate matter can be formed as a result of chemical reactions; for example, ozone created by an electronic air cleaner reacting with the terpenes ("scent" chemicals in cleaning products) to form UFP.
 - Disassociation into gaseous constituents can occur under certain circumstances. For example, when the particles are brought into an indoor environment, ammonium nitrate particles from outdoor air can dissociate into their gaseous constituents (nitric acid and ammonia), which can cause a significant net loss of airborne particle mass (Nazaroff 2004)

Regardless of the type or age of a building, good IAQ starts with implementing three primary strategies for controlling indoor air contaminants: ventilation, air filtration or cleaning, and source control

- Ventilation. A well-designed and properly operating HVAC system not only conditions indoor air, but also dilutes indoor air pollutants and transports them outside. In addition, the HVAC system is invaluable for maintaining appropriate building pressurization, which is crucial for preventing infiltration of outdoor air particles through the building envelope or windows. Even the most efficient HVAC system, however, will bring in some outdoor air pollutants and particles via supply air or have contaminants created from indoor sources which enter the airstream via return air. To mitigate these eventualities, air filters and cleaners have become a vital part of HVAC system design.
- **Filtration.** The two primary methods of capturing particles are mechanical or electronic filtration. The ability of common ventilation air filters to capture UFP varies with particle size distribution. For example, mechanical filtration works best at capturing large (> 0.5 μ m) or very small particles (< 0.2 μ m). Because of the opposing trends in how large and very small particles behave in the air stream, mechanical filters are less efficient at

capturing particles measuring between 0.1 μ m to 0.4 μ m. Air molecules heavily influence the motion of UFP in the air stream. As a result, the particles' motion around their basic path becomes random. Air traveling at lower velocities provides more time for these small particles to move away from their primary path through the air stream and increases their chances of being caught and held. This process is called *diffusion*, and is the key factor in the how high efficiency particle air (HEPA) filters remove UFP from the air (McDonald and Ouyang 2000, Eckberg and Shi 2009).

Pre-filters and HEPA filters will filter particles as small as 1 μ m in diameter or less, but with varying efficiencies. Ultra low penetration air (ULPA) filters are like an ultra-HEPA filter, which are designed to capture 99.9995 percent of all airborne particles measuring 0.12 μ m in diameter or larger. By installing class F7 filters (classified according to the European standard EN779), removing about 75 percent of the total number of UFP should be possible (Penn State 2006, AHAM 2006, Ekberg and Shi 2009).

Electronic filtration devices use electrostatic forces to trap particles. In commercial or industrial applications, these devices are referred to as charged media precipitators or electrostatic precipitators. In residential applications, they are called electronic air cleaners, some of which are portable and can be moved from room to room. The simplest form of electronic air cleaner is the negative ion generator, which uses static charges to make the particles larger, which caused them to settle out of the air faster (Penn State 2006). These less sophisticated models have a significant disadvantage in that by charging the particles in a room, the particles can become attracted to and deposit on surfaces such as walls, floors, tabletops, and curtains (ALA Special Report on Air Cleaners).

Some room air cleaners have used ozone to remove odors while leaving a fresh, clean smell like after a thunderstorm. Research has shown, however, that these types of air cleaners or purifiers are not particularly effective and in fact may be hazardous to health (Underhill 2000). Ozone is a very strong lung irritant, which can cause or exacerbate respiratory disease. As noted above, it can react with VOCs to produce additional VOCs such as aldehydes, which have a more unpleasant odor, are far more irritating, and are more toxic than other VOCs in the indoor air (Boeniger 1995). It also can react with VOCs, such as terpenes, to form UFP.

Other air cleaners are designed to remove gases, vapors, and odors as well as particulates. This removal process, called *adsorption*, is relatively simple in that air passes through an adsorption bed(s), which filters out the gases, vapors, and odors. Adsorption beds are made up of *sorbents*. Solid sorbents, such as activated carbon, are especially useful for removing diesel fumes, hydrocarbons, ETS, body odor, cooking odors, and high-molecular weight VOCs.

Source control. By far the most effective way to minimize exposure of indoor air
pollutants is to control their sources. Using building materials that emit low or no VOCs
removes a key component in creating UFP. Another strategy is to select electronic
products (computers and displays), printers, and multifunction devices that are certified
to be low particle and low VOC emitters. Local exhaust vented to the outside can assist
in the removal of particles from active sources such as cooking, grilling, oven cleaning,

bathroom cleaning and the use of certain consumer products. Adding outdoor air ventilation can also help flush UFPs out as they are created or even dilute their concentration to some degree.

Product certification

Product Certification programs are available to qualify products for low emissions of VOCs, formaldehyde, and particles. Several organizations in the US and Europe have established "ecocriteria" for acceptable levels of airborne contaminants emitted from printers, copiers, and other types of electronic products. These international programs include Germany's Blue Angel Program, the UL GREENGUARD Certification Program, and the Japan Electronics and Information Technologies Association (JEITA). . Table 7 provides a summary of these eco-criteria, and several have included criteria for UFP.

ECMA International, an international industry association dedicated to the standardization of consumer electronics has, for the first time, incorporated the measurement of UFP in their standard test method for measuring emissions from electronic equipment (ECMA-328).

Table 7. Summary of Eco-Criteria for Acceptable Levels of Airborne Contaminants

| Organization | Standard | Product Category | TVOC / VOC Criteria | Formaldehyde Criteria | Particulate Criteria | Testing Standards |
|-----------------------------|------------|--|---|--------------------------|--|--|
| The Blue Angel (Germany) | RAL-UZ 171 | Printers, copies and multifunction devices | Ozone: Monochrome: ≤ 1.5 mg/h Color: ≤ 3.0 mg/h TVOC: Monochrome: ≤10 mg/h Color: ≤18 mg/h Unidentified single VOCs: Monochrome: ≤ 0.9 mg/h Color: ≤ 0.9 mg/h Color: ≤ 0.05 mg/h Color: ≤ 0.05 mg/h Styrene: Monochrome: ≤1.0 mg/h Color: ≤1.8 mg/h | None specified | Dust: Monochrome: ≤ 4.0 mg/h Color: ≤ 4.0 mg/h Ultrafine: 3.5x10 ¹¹ [particles/10 min] (monochrome and color) | RAL-UZ 171, Appendix 2 GGTM.P058/UL 2819 ISO/IEC 28360:2007 |

| Organization | Standard | Products Covered | TVOC / VOC Criteria | Formaldehyde Criteria | Particulate Criteria | Testing Standards |
|--|---|---|--|---|--|----------------------|
| Organization Standard UL GREENGUARD GGPS.003 GREENGUARD/UL 2819 | Printers, copies and multifunction devices | Emission Rate Ozone: Monochrome: ≤ 1.5 mg/h Color: ≤ 3.0 mg/h TVOC: Monochrome: ≤ 10 mg/h Color: ≤18 mg/h Benzene: Monochrome: ≤ 0.05 mg/h Color: ≤ 0.05 mg/h Styrene: Monochrome: ≤1.0 mg/h Color: ≤ 1.8 mg/h | Emission Rate Monochrome: 1.2 mg/h Color: 1.2 mg/h | Emission Rate Total Dust: Monochrome: ≤ 4.0 mg/h Color: ≤ 4.0 mg/h | RAL-UZ-171, Appendix M ISO/IEC 28360:200 GGTM.P058 | |
| | | | Room Concentration Ozone: Monochrome: ≤ 0.06 mg/m³ Color: ≤ 0.13 mg/m³ TVOC: Monochrome: ≤ 0.4 mg/m³ Color: ≤ 0.8 mg/m³ Benzene: Monochrome: ≤ 0.002 mg/m³ Color: ≤ 0.002 mg/m³ Styrene: Monochrome: ≤ 0.04 mg/m³ Color: ≤ 0.08 mg/m³ Individual VOCs: Monochrome: ≤ 0.1 TLV Color: ≤ 0.1 TLV | Room Concentration Monochrome: ≤ 0.05 mg/m³ Color: ≤ 0.05 mg/m³ | Room Concentration Respirable Particles: Monochrome: ≤ 0.15 mg/m³ Color: ≤ 0.15 mg/m³ Total Dust: Monochrome: ≤ 0.16 mg/m³ Color: ≤ 0.16 mg/m³ | |

Table 7. Summary of Eco-Criteria for Acceptable Levels of Airborne Contaminants (cont'd)

| Organization | Standard | Products Covered | TVOC / VOC Criteria | Formaldehyde Criteria | Particulate Criteria | Testing Standards |
|--------------|--|-------------------------------------|---|---|--|---|
| | GGPS.004 GREENGUARD Standard | Consumer Electronic equipment | TVOC: Short term ≤ 5.0 mg/m³ Long term ≤ 0.22 mg/m³ Ozone: Long term ≤ 0.05 ppm | Short term ≤ 0.040 ppm Long term ≤ 0.013 ppm | PM 2.5 Long-term chronic: ≤ 0.035 mg/m ³ | GGTM.P072 |
| JEITA | VOC Guideline for Personal Computers, Version 2 | Personal computers, monitors | See Table 8 added below | None specified | None specified | ISO/IEC 28360 ISO 16000-3 ISO 16017-1 |

Table 8. JEITA VOC Guidelines for Personal Computers

| [Unit: µg/(h·unit)] | Laptop PC | All-in-One PC | Desktop PC*2 | Display*2 |
|---------------------|-----------|---------------|--------------|-----------|
| Substance | | | | |
| Toluene | 260 | 260 | 130 | 130 |
| Xylene | 870 | 870 | 435 | 435 |
| p-Dichlorobenzene | 240 | 240 | 120 | 120 |
| Ethylbenzene | 3800 | 3800 | 1900 | 1900 |
| Styrene | 220 | 220 | 110 | 110 |
| Tetradecane* | 330 | 330 | 165 | 165 |
| Formaldehyde | 100 | 100 | 50 | 50 |
| Acetaldehyde | 48 | 48 | 24 | 24 |

^{*}Optional

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