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Title: Ultrafine particle emission from floor cleaning products

Running title: UFPs and cleaning products

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Abstract

The new particle formation due to the use of cleaning products containing volatile organic compounds (VOCs) in indoor environments is well documented in the scientific literature. Indeed, the physical-chemical process occurring in particle nucleation due to VOC-ozone reactions was deepened as well as the effect of the main influencing parameters (i.e. temperature, ozone). Nonetheless, proper quantification of the emission under actual meteo-climatic conditions and ozone concentrations is not available.

To this end, in the present paper the emission factors of newly-generated ultrafine particles due to the use of different floor cleaning products under actual temperature and relative humidity conditions and ozone concentrations typical of the summer periods were evaluated. Tests in a chamber and in an actual indoor environment were performed measuring continuously particle number concentrations and size distributions during cleaning activities.

The tests revealed that a significant particle emission in the nucleation mode was present for half of the products under investigation with emission factors up to 1.1×10^{11} part. m⁻² (8.8×10^{10} part. mL_{product}⁻¹), then leading to an overall particle emission comparable to other well-known indoor sources when cleaning wide surfaces.

Keywords: nucleation; indoor air quality; cleaning products; ultrafine particles; FMPS.

Practical Implications: The study provided useful data in view of a more detailed knowledge of the possible particle sources in indoor environments. The emission factor data here reported could help to simulate different scenarios to assess the exposure to ultrafine particles of both cleaning personnel and non-professional users.

Conflict of Interest: The authors have no conflicts of interest to declare.

1. Introduction

House cleaning aims to provide a level of hygiene that promotes health and productivity. However, the cleaning activities are not necessarily related to an adequate indoor air quality. Indeed, cleaning is known to be a source of air pollutants and several studies have shown that airway effects (e.g. asthma, rhinitis) can be associated with the use of household cleaning products both in cleaning personnel and non-professional users ¹⁻⁶. The effect of

the exposure to cleaning agents is even more critical for children and adolescents as they have a higher risk of respiratory and allergic diseases ^{7,8}.

The presence of air pollutants related to the use of cleaning products is due to the ozone-initiated reactions of volatile organic compounds (VOCs), such as terpenes and terpenoids (e.g. d-limonene) ⁹⁻¹⁴, and glycol ethers ¹⁵ included in the cleaning product composition. The ozone-VOCs interactions produce new oxygenated volatiles, e.g. formaldehyde and acetaldehyde ^{11,13,16,17}, and some multi-oxygenated compounds (e.g. dicarbonyls, peroxides) that may condense forming ultrafine secondary organic aerosols (SOAs) ^{14,18-23}. Then, based on the residence time of such SOAs in indoor (which is a function of the air exchange rate of the environment) and the intensity of the SOA formation, the newly-generated particles may also adsorb/condense onto pre-existing particles ⁹.

Thus, the presence of ozone (O_3) is essential for the formation of such secondary pollutants. Different studies found that the higher the ozone concentrations the higher the number of secondary particles generated ^{9,24}. The ozone concentration in indoor environments is driven by the possible presence of ozone sources and the outdoor-to-indoor penetration. The main indoor O_3 sources are printers and photocopiers ²⁵ and air cleaning devices ²⁶, whereas negligible contributions are due to other devices like computers ²⁷. Nonetheless, in most of the cases, the indoor O_3 concentrations are mainly affected by the outdoor-to-indoor penetration with values typically ranging from 0.3 to 0.7 of outdoor levels according to the ventilation conditions; typically higher values were measured for ventilation strategies relying upon windows opening ²⁸⁻³². Actually, the outdoor ground level ozone concentrations are not constant, indeed, variation on hourly, daily, and season basis are expected since O_3 is not emitted directly into the air, but it is generated by chemical reactions between oxides of nitrogen (NO_x) and VOCs in the presence of sunlight. Thus, higher outdoor (and, then, indoor) O_3 concentrations are expected in the sunniest hours of the summer days ³³⁻³⁵.

The SOA formation in outdoor environments has been widely deepened by the scientific community ³⁶⁻³⁹ to such an extent that the contribution of such SOAs to the overall $PM_{2.5}$ or PM_{10} fractions in cities was also determined ^{40,41}. On the contrary, a gap of knowledge still exists for indoor environments. Indeed, even if the physical-chemical process involving the indoor formation of SOA is well known ^{11,13,19}, as well as the effect of the main influencing parameters ⁴², no studies were performed to quantify the emission of the SOA indoor sources. This is even more important for number-based aerosol metrics, because the contribution of very small particles formed via nucleation on mass-based aerosol metrics, i.e. PM fractions, is expected to be negligible; as an example, the SOA contribution in indoor environments in terms of $PM_{2.5}$ was detected as low as <3% ⁴³. Moreover, most of the studies investigating the indoor generation of SOAs from VOC-ozone interaction were performed in controlled chamber under meteo-climatic conditions and ozone concentrations reproduced ad-hoc in order to emphasize the nucleation phenomena but that could differ from the actual indoor environment conditions and the actual use of household cleaning products ^{9,44,45}.

In the present study, the quantification of the secondary ultrafine particle emission due to the use of floor cleaning products in actual indoor conditions was performed. In particular, an experimental campaign was carried out to evaluate the emission factors of newly-generated particles (around 10 nm in diameter) of twenty different cleaning products under temperature, relative humidity and ozone concentrations typical of the summer period in Italy. To this end, continuous measurements of particle number concentrations and size distributions were carried out both in a test chamber and in an actual indoor environment.

2. Materials and methods

2.1. Description of the cleaning products and of the measurement site

In order to provide representative data, the study was performed using 20 floor cleaning products manufactured by large national and international companies and readily available for purchase online and in most supermarkets in Italy. In particular, the floor cleaners were selected based on the market shares and sale data of the products. Indeed, the authors selected products whose brands account for more than 80% of the total market share of cleaning products for large surfaces. The characteristics of the twenty floor cleaners selected are summarized in Table 1: the chemical composition (to the extent that it is specified) of each product is reported as well as the dilution ratio suggested by the manufacturers. On the basis of the information provided on the chemical composition, most of the cleaning products presented VOCs (e.g. terpenes), salts, and surface agents which could affect the particle formation phenomena. Nonetheless, the information provided are just qualitative since the concentration of such compounds are not provided. Four products (Q, T, U, V) are promoted, and then classified, as eco-friendly cleaners as they are certified with the EU Eco label due to their reduced health and the environment impact during preparation (e.g. prepared only with vegan components, reduced plastic packaging).

2.2. Site description

The experimental analyses were performed on August–October 2019 in a 150-m³ laboratory room of the European Accredited (EA) Laboratory of Industrial Measurements of the University of Cassino and Southern Lazio, Italy, in a naturally ventilated 4.7 m³ chamber (1.80 m × 1.20 m × 2.20 m) with walls made up of Plexiglas. The ventilation conditions of the laboratory room were held constant during the tests; indeed, windows were kept open and doors were kept close during the tests and the mechanical ventilation system was turned off.

Since meteo-climatic conditions and ozone levels may affect the possible particle formation via nucleation, temperature (T), relative humidity (RH) and ozone (O₃) levels during the entire experimental analysis were logged: in particular, temperature and relative humidity inside the test chamber were measured continuously through a portable Thermo-Hygrometer Datalogger, whereas hourly-average outdoor ozone concentrations were provided by the Italian environmental protection agency through the fixed sampling station located in the city (Cassino).

In order to perform measurements in quite similar conditions, the tests were performed on sunny days in the time period 10.00 a.m. - 4.00 p.m. In fact, T, RH and O₃ levels during the entire experimental analysis resulted quite constant as highlighted by the values summarized in Table 2, where average values were reported along with the standard deviations. Average temperature and relative humidity values were equal to 26.0 °C and 48.6%, with standard deviation of 0.9 °C and 3.9%, respectively, then in a range not inhibiting the SOA formation via nucleation⁴². The outdoor O₃ concentrations also resulted quite constant during the measurement periods (average value 117 µg m⁻³, standard deviation 15.1 µg m⁻³). As mentioned above, even if indoor O₃ concentrations were not measured, the outdoor value can provide a good estimate of the indoor values when no indoor sources are present (as in the room where the tests were performed) and indoor-to-outdoor concentration ratio is increased opening the windows^{32,43}.

2.3. Methodology

In order to quantify the new particle formation via nucleation process, the emission factors in the nucleation size range as a function of the unit cleaned floor surface (EF_{fs} , part. m^{-2}) and of the mL of product (EF_{mL} , part. mL^{-1}) were evaluated. To this end, particle number concentrations and size distributions were measured simultaneously during the cleaning events through a butanol-based Condensation Particle Counter (CPC 3775, TSI Inc.) and a Fast Mobility Particle Sizer (FMPS 3091, TSI Inc.). The CPC 3775 is able to measure the number concentration of particles down to 4 nm in diameter up to $1 \times 10^7 \text{ part. cm}^{-3}$ with 1-s sampling time and a sampling flow rate of 1.5 L min^{-1} , whereas the FMPS 3091 is able to measure the particle size distributions with size resolution of 16 channels per decade, i.e. 32 equally sized bins in the size range of 5.6 to 560 nm, with 1 s time resolution and a sampling flow rate of 10 L min^{-1} . The instruments were placed outside the chamber and sampled aerosol from the chamber through very short tubes in order to avoid particle diffusion losses on the inner surface of the tubes.

The evaluation of the EF values was carried out averaging over three measurements for each cleaning product. Each measurement was performed with the following procedure: a) 10 min of background measurement in the chamber (with no products), b) on the tenth minute of measurement, 100 mL of mixture of water and cleaning product (according to the dilution ratio suggested by the manufacturer) were spread over 1 m^2 of chamber floor and left it to dry. The measurements were performed continuously with 1-s sampling frequency and were stopped when the particle concentration decayed to the background values (if any nucleation process occurred) or, at least, 1 h after the cleaning event started. The mixtures were prepared using beakers and lab bottles marked with volume measurements. In particular, for each product the mixture was prepared as follow: 1 L of water was poured in a bottle, then the cleaning product was added according to the suggested dilution ratio, finally the mixture was stirred in order to homogenize it. Then, for each test, 100 mL of mixture were extracted with beaker marked with volume from the main bottle.

From the particle size distribution trends obtained from the FMPS data, the particle generation for each particle size could be detected. In particular, since the nucleation events occur at a mode around 10 nm, as hereinafter discussed in the Results section, the quantification of the emission was performed considering the size bins with midpoints ranging from 8.1 to 12.4 nm (hereinafter defined “8-12 nm” size range or “nucleation mode”). The emission factor for the unit wetted surface (EF_{fs} , part. m^{-2}) of 8-12 nm particles was evaluated considering the simplified mass-balance particle equation previously applied for several indoor sources^{46–49}:

$$EF_{fs} = V \left[\frac{C_{in} - C_{in,0}}{\Delta t} + (\overline{AER} + k) \cdot \overline{C_{in}} - AER \cdot C_{in,0} \right] \cdot \Delta t \quad (1)$$

where C_{in} and $C_{in,0}$ represent the peak and initial (background) indoor particle concentrations in the nucleation mode, respectively, Δt is time difference between initial (i.e. the starting time of the cleaning activity) and peak concentration, AER is the air exchange rate (as obtained through the CO_2 decay test), $\overline{AER} + k$ is the average total removal rate due to both particle exfiltration (related to the AER) and particle deposition (evaluated by means of the particle deposition rate, k), $\overline{C_{in}}$ is the average indoor particle concentration in the room, and V is the volume of the room. As mentioned above the eq. (1) is a simplified version mass-balance equation as it was derived considering constant generation rate, removal rate, and AER over time. A further main assumption adopted is considering negligible the nucleation, evaporation and coagulation phenomena; in our study this is clearly not true since our aim was to measure the new particle formation through nucleation and, moreover, particle growth phenomena are expected due to the presence of many new generated very small

particles that could either quickly coagulate with each other and slightly more slowly deposit on the surface of larger particles^{9,50,51}. Nonetheless, our aim was to quantify the emission of new particles in a very narrow size range, thus (i) the nucleation in the 8-12 nm range is the source that the authors are quantifying, (ii) the possible coagulation or absorption of newly formed particles onto larger particles (outside the 8-12 size range) will be included in the particle deposition rate (k). Thus, the eq. (1) can be considered suitable for the evaluation of the emission of 8-12 nm particles via nucleation.

The AER value was obtained on the basis of an experimental characterization of the test-chamber; in particular, a tracer gas decay test⁵² was applied using a CO₂ bottle and a non-dispersive infrared analyzer (Testo - Ambient CO₂ probe). Specifically, five CO₂ decay tests were performed. The AER tests were performed measuring the CO₂ concentration decay after having increased the CO₂ level in the chamber up to roughly 2000 ppm. The mean AER resulted equal to 0.12 h⁻¹. This is a value typical of naturally ventilated indoor environments when doors and windows are kept close^{53,54}. In order to properly evaluate the actual AER occurring during the test, the contribution of the instrument flow rate was also added (11.5 L min⁻¹), then leading to an AER value adopted in the eq. (1) of 0.27 h⁻¹.

The average total removal rate, $\overline{AER + k}$, was evaluated for each test as average decay rate of indoor particle concentration after the indoor activity ceased (i.e. after having reached the concentration peak); in particular, it was calculated as coefficient of the exponential regression typical of the particle concentration exponential decay as applied in previous papers^{46-49,55}. The authors point out that a correct evaluation of the emission factor is affected by the spatial uniformity of the ultrafine particle concentration in the chamber; actually, this is not a big issue in the experimental campaign here performed since the source is quite spread (1 m² floor surface) and the chamber volume is small, then promoting a quick spatial homogenization of the particle concentration in the chamber.

The emission factor of the mL of product (EF_{mL}, part. mL⁻¹) was evaluated multiplying the EF_{fs} (part. m⁻²) by the quantity of product employed to clean the 1 m² floor surface. The authors highlight that the two different emission factors (EF_{fs} and EF_{mL}) were provided in order to help the readers in extrapolating the data in the more convenient form. Indeed, while information on the dilution ratios are provided by the manufactures, no data on the amount of product needed to clean a certain floor area are provided. Thus, to clean a unit floor area people could employ a mixture volume lower or higher than the 100 mL considered in the present paper.

As regard the instrumentation adopted in the experimental analysis, we point out that the concentration trend of the nucleation mode was obtained from the FMPS 3091 particle size distribution. Actually, in previous papers the FMPS was recognized frequently overestimating or underestimating the particle concentration due to its particle charging efficiency, that can be not effective with pre-charged aerosols (e.g. combustion-generated particles), and its simplified counting technique (electrometers)⁵⁶⁻⁵⁸. This is the reason why, in order to check the accuracy of FMPS in measuring total particle number concentrations, the total particle number concentration was simultaneously monitored using the CPC.

2.4. Experiments in an actual indoor environment

In order to show the possible secondary particle formation in an actual indoor environment, two further cleaning experiments were performed: in particular, tests with an emitting product (product B) and a non-emitting product (product N) were performed in a naturally ventilated room (office) of 40 m³ (13 m²) of the Laboratory of Industrial Measurements (LAMI). The tests were performed adopting the same methodology considered in the chamber experiments. Indeed, after 10 min of background measurements, the cleaning activity was started. The same suggested dilution ratios of the mixtures and same mixture volume for

unit floor area of the chamber test (100 mL m^{-2}) were considered. Since the FMPS 3091 provided good results in estimating the particle number concentration for the specific aerosol under investigation in the chamber tests (please see result section 3.1), in the actual indoor environment tests, the continuous measurements (1-s sampling frequency) were only performed through the FMPS (which was located inside the office). The ventilation conditions of the room were held constant during the tests; indeed, windows were kept open and doors were kept close. During the experiments, indoor temperature and relative humidity as well as outdoor ozone concentration were logged. In particular, quite constant temperature (average 26.7°C , standard deviation 0.3°C), relative humidity (average 47.8% , standard deviation 2.0%) and outdoor O_3 concentrations (average $101 \mu\text{g m}^{-3}$, standard deviation $3.2 \mu\text{g m}^{-3}$) were detected; these values are also similar to those measured during the chamber experiments.

3. Results and discussions

3.1. Particle number concentration and distribution trends

In Figure 1 an illustrative example of particle number concentration trends measured through the FMPS 3091 for one of the three tests performed for product A and product V is reported. In particular, the total particle number concentrations over the entire size range ($5.6\text{-}560 \text{ nm}$) and the particle concentration in the nucleation mode ($8\text{-}12 \text{ nm}$ size range) are reported. The concentration trends clearly highlighted two different behaviors: in particular, after having spread the water-cleaning product mixture (at $t=10 \text{ min}$), the total concentration and nucleation mode concentration of the product A started increasing after roughly less than 1 min , whereas no increases were recognized for product V. The $8\text{-}12 \text{ nm}$ concentration trend of the product A reached a peak after two minutes (at $t=12 \text{ min}$; in this test $\Delta t=2 \text{ min}$), then a decrease occurred and the concentration dropped down to the background level in few minutes after the peak. Such an increase of the $8\text{-}12 \text{ nm}$ size range concentration clearly evidenced a new particle formation due to the co-presence of favorable boundary conditions (i.e. T , RH , O_3 level) leading to nucleation events. The total particle number concentration also increased; anyway, even during the concentration decrease of the $8\text{-}12 \text{ nm}$ size range, the total particle concentration remained quite high for several minutes before starting decreasing. This is clearly due to the quick coagulation of such small newly generated particles (forming larger particles) and/or the consequent deposition on the surface of larger pre-existing particles. These processes lead to a reduction of the $8\text{-}12 \text{ nm}$ concentration and an increase of larger particle concentrations. Indeed, the total removal rate $\overline{AER + k}$ of the particles in the nucleation mode was very high with respect to the typical deposition rates⁵⁵ (15 h^{-1} for the test under discussion) since the contribution of the AER alone is very limited (the average AER resulted equal to 0.12 h^{-1} , please see section 2.3). This is clearly evidenced in Figure 2 and Figure 3 where the temporal evolution of particle size distributions of the two illustrative examples reported in Figure 1 are shown. In particular, the temporal evolution of the particle size distribution for the product A test (Figure 2a and Figure 3a) demonstrates that the background particle size distribution (just before the cleaning activity started) presents a mode around $70\text{-}80 \text{ nm}$ but, as soon as the nucleation event occurred, an increase of the 10 nm mode was detected ($t=12 \text{ min}$). Then, the nucleation mode started decreasing and an increase of particles of 20 nm happened due to coagulation processes. Actually, the evolution of the coagulation leads to a further increase of the particle distribution mode (towards 30 nm) and a simultaneous decrease of the total particle concentration. Due to the abovementioned quickly coagulation of small particles with each other and the slightly more slowly deposition on the surface of larger particles, the decays of total particle number concentration and $8\text{-}12 \text{ nm}$ size range concentration are not

simultaneous, indeed, the decrease in concentration of the 8-12 nm size range particles resulted faster than the total concentration one. On the contrary, the evolution of the particle size distribution of the test performed on the product V (Figure 2b and Figure 3b), does not show any change in the distribution since no new particle formation phenomena were observed: indeed, all the distributions were unimodal with a peak at about 70 nm.

The two tests discussed in details were reported as illustrative examples since all the tests performed on the 20 cleaning products were similar to the product A, i.e. with nucleation phenomena, or to the product V, i.e. with no new particle formation; thus, on the basis of their concentration and distribution trends, the 20 cleaning products can be defined as emitting or non-emitting. In particular, emitting products presented different peak concentrations (ranging from 0.9×10^3 to 2.99×10^4 part. cm^{-3}), Δt (ranging from less than 2 min to 15 minutes) and total removal rates (from 1.7 to 15.4 h^{-1}) then leading to the different emission factor values hereinafter discussed.

3.1.1. Correlation between FMPS and CPC measurements

The particle concentration and distribution data of the tests performed with product A and V reported in the previous section, were obtained from the FMPS 3091 measurements. Nonetheless, as reported in the methodology section, simultaneous measurements of total particle number concentration were performed with the CPC 3775 due to its higher accuracy in particle counting (in particular for certain aerosols). In order to evaluate the reliability of the FMPS 3091 in measuring the total particle number concentrations, in Figure 4 the correlations amongst the total particle number concentrations measured by the FMPS and CPC for the two tests analyzed (product A and V) are reported. The graphs clearly highlight a good correlation amongst the two instruments with no particular under- or over-estimates of the concentrations when using the FMPS (differences of $\pm 5\%$ with respect to the CPC in the two illustrative examples discussed in detail). Indeed, when considering all the tests performed on the 20 products, the FMPS total concentrations were from 0.93-fold to 1.08-fold the CPC ones. This good agreement amongst the instruments is maybe due to the fact that the newly-generated particles did not present a pre-charge distribution as typically occurs for combustion generated particles^{56–58}. Due to the reliability of the FMPS in measuring the total concentrations, the data hereinafter reported and the emission rates/factors evaluated were obtained from the FMPS measurements.

3.2. Emission factors

In Table 3 the emission factors expressed as amount of particle generated per unit floor surface (EF_{fs} , part. m^{-2}) and per unit product (EF_{mL} , part. $\text{mL}_{\text{product}}^{-1}$) are reported. Ten of the twenty cleaning products investigated were identified as “emitting” (A, B, C, D, E, F, G, H, I, O), whereas the other ten products (L, M, N, P, Q, R, S, T, U, V) did not show recognizable peaks in concentrations during the tests and, consequently, were identified as non-emitting products.

The average emission factor values for emitting products ranged from 1.5×10^9 part. m^{-2} and 1.3×10^9 part. $\text{mL}_{\text{product}}^{-1}$ to 1.1×10^{11} part. m^{-2} and 8.8×10^{10} part. $\text{mL}_{\text{product}}^{-1}$ in terms of EF_{fs} and EF_{mL} , respectively. Therefore, cleaning an entire house would cause a very high emission of particles via nucleation, indeed, considering the average floor area of newly built houses in Italy, 88 m^2 (Italian National Statistical Institute, ISTAT 2018, www.istat.it), a total emission up to 9.3×10^{12} particles can be reached. This emission is typically lower than other indoor sources involving combustion activities (i.e. 1 h of cooking activities (Buonanno et al., 2009, 2011), 1 h of incense and candle combustion⁶¹, etc.) but it is comparable to or larger than some non-combustion indoor sources like 1 h of 3D printing⁴⁹ or laser printing⁴⁸.

An in-depth analysis of the emission factors on the basis of the chemical composition of the different products is extremely hard to be carried out. As an example, both emitting and non-emitting products presented VOCs in their composition: thus, the amount of such VOCs in the products is a key information to provide possible correlation with the emission factor data. Moreover, a further effect on particle nucleation could be due to the presence of non-ionic surface agents and salts as they can affect the gas-to-particle conversion phenomena due to their role on surface tension and evaporation processes⁶²⁻⁶⁴. Nonetheless, once again, more detailed information on the type and concentration of surface agents and salts (generic information was only provided by the manufacture, i.e. <5%) would help to understand and quantify their roles in the formation of ultrafine particles.

The results in terms of emission factors obtained from the experiments performed in the chamber represent key data in exposure assessment studies. In fact, such values could be easily used to simulate the exposure in an indoor environment where cleaning activities are performed under different scenarios (in terms of ventilation, type of product, floor area, etc.) using both simplified mass-balance particle equations or more complex CFD models.

3.3. Results of the experiments in an actual indoor environment

In order to check the transferability of the results obtained in the chamber to actual environments, results referred to an actual indoor environment described in the section 2.4 are here reported. In particular, in Figure 5 the trends of particle number concentration of the tests performed using the product B (recognized as emitting product) and product V (recognized as non-emitting product) are described. In particular, both the total particle number concentration over the entire size range (5.6-560 nm) and the particle concentration in the nucleation mode (8-12 nm size range) are shown. As expected, the trends of the two products were different: the trends of the non-emitting product (N) resulted flattened both in terms of nucleation range and entire size range indicating that no new-particle formation phenomena occurred. On the contrary, the trends of the emitting product (B) increased after few minutes the cleaning event started. In particular, the particle concentration of the nucleation range (8-12 nm) reached a peak (about 3.6×10^3 part. cm^{-3}) at $t=21$ min and then started decreasing, whereas the total particle number concentration peak was reached few minutes later ($t=23$ min) due to the abovementioned coagulation of such small newly generated particles (forming larger particles) and/or the consequent deposition on the surface of larger pre-existing particles.

These phenomena are clearly recognizable in Figure 6 where the temporal evolution of particle size distributions, reported as contours plots, for the tests carried out with product B and N are reported. In particular, the particle distributions measured during the test carried out with the product B clearly highlight a particle formation at about 10 nm and a consequent shift of the mode toward larger particles. With respect to the tests carried out in the chamber, here a slower decay in the nucleation range particle concentration and a less pronounced shift of the mode were recognized due to the larger volume available for the newly-generated particles which mitigates the coagulation phenomena. Indeed, comparing the 8-12 nm particle concentration and distribution trends for product B in the actual environment and for product A in the chamber (Figure 1) clearly shows up that, despite the quite similar emission factors the two products (Table 3), the peak concentration measured in the actual environment test resulted lower, and, consequently, the following coagulation phenomena resulted less severe.

Summarizing, the two tests performed in the actual environment supported the quantitative findings obtained with the tests performed in the chamber.

4. Conclusions

In the present study, for the very first time, the emission of newly-generated ultrafine particles when using floor cleaning products was measured. To this end, tests in a chamber and in actual indoor environment were performed under actual temperature and relative humidity conditions and ozone concentrations typical of the summer period.

Tests in the chamber were performed on 20 different products (mostly containing VOCs and surface agents). Ten out twenty cleaning products were recognized as emitting products since a generation of particles in the nucleation range (about 10 nm) was measured, whereas the other ten products did not show any particle generation. The emission factor of the emitting products ranged between 1.5×10^9 part. m⁻² (1.3×10^9 part. mL_{product}⁻¹) and 1.1×10^{11} part. m⁻² (8.8×10^{10} part. mL_{product}⁻¹) then leading to a total particle emission comparable to other well-investigated indoor sources when cleaning the entire floor area of a typical dwelling.

Although the chamber tests were performed under actual parameters (i.e. temperature, relative humidity and ozone concentration), further tests were extended to an actual indoor environment. In particular, two tests were performed, with an emitting and a non-emitting product, in 40 m³ room under temperature and relative humidity conditions and ozone concentrations typical of the summer period (and then similar to those obtained in the chamber test). The results of these tests confirmed the behaviors measured in the chamber test.

Summarizing, the study provided interesting findings in view of a more detailed knowledge of the possible particle sources in indoor environments; indeed, the emission factor data here reported could help to simulate different scenarios to assess the exposure to ultrafine particles of both cleaning personnel and non-professional users. Indeed, even if the emission rates are typically not as high as than those due to the use of indoor combustion sources, quite high concentrations for prolonged periods can occur and this could represent a potential health concern since the toxicology of such freshly-emitted particles is basically unknown. Therefore, further studies should go in the direction of (i) investigating the effect of chemical composition on the particle emission performing ad-hoc chemical analyses of the products in order to obtain detailed compositions that were not available in the present study and (ii) characterizing the chemical composition of the newly-generated particles in order to assess their possible health effect.

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Tables

Table 1 - Composition of the products investigated and dilution ratios suggested by the manufacturer.

cleaning products	composition of the product	dilution ratio (mL _{product} mL _{water} ⁻¹)
A	Alcohols, C9-11-branched, Ethoxylated, Sodium laureth sulfate, Ethanol, Parfum, Diethylenetriaminopentamethylenphosphonic acid, Sodium salt, Sodium citrate, Isopropyl alcohol, Citral, Geraniol, Hexyl cinnamal, Amyl cinnamal, Limonene, Colorants, Methylchloroisothiazolinone, Methylisothiazolinone	0.012
B	Sodium C10-13 Alkyl-benzenesulfonate, Parfum, Deceth-8, Sodium laureth sulfate, Sodium chloride, Limonene, Glutaral, Styrene/Acrylates Copolymer, Citral, Sodium citrate, Citronellol, Colorants	0.012
C	<5% non-ionic surface agents, soap, Glutaral, Benzisothiazolinone, Parfum, Citral, Citronella, Hexyl cinnamal, Limonene, Linalool	0.012
D	<5% non-ionic surface agents, Parfum, Limonene, Citral, Benzisothiazolinone	0.012
E	<5% non-ionic surface agents, <5% cationic surface agents, <5% EDTA disodium salts. Other components: Parfum, Benzisothiazolinone, Amyl Cinnamal, Cynamyl Alcohol, Geraniol, Limonene, Linalool	0.0125
F	<5% amphoteric surface agents, <5% non-ionic surface agents, Parfum, benzalkonium chloride, Benzisothiazolinone, Methylisothiazolinone	0.012
G	Sodium C10-13 Alkyl-benzenesulfonate, Deceth-8, Parfum, Sodium laureth sulfate, Sodium chloride, Hexyl Cinnamal, Linalool, Glutaral, Citronellol, Benzyl Salicylate, Sodium Citrate, Colorants, Limonene	0.012
H	<5% 2-methyl-2H-isothiazol-3-one, Benzisothiazolinone, Parfum, soap, non-ionic surface agents, Limonene, Hexyl cinnamal, Alpha isomethyl ionone	0.012
I	<5% non-ionic surface agents, Parfum, Benzyl salicylate, Limonene, Amyl cinnamal, Linalool	0.010
L	<5% parfum, Benzisothiazolinone, Methylisothiazolinone, non-ionic surface agents, Limonene, Linalool	0.012
M	benzalkonium chloride, <5% non-ionic surface agents, cationic surface agent, parfum, Limonene, Geraniol.	0.0125
N	<5% non-ionic surface agents, Parfum, Benzisothiazolinone	0.0125
O	Limonene, Linalool, Citral, Benzisothiazolinone, Parfum, Limonene, Linalool, Citral	0.012
P	<5% non-ionic surface agents, cationic surfactant, soap, optical brighteners, parfum, Benzyl Salicylate, Methylchloroisothiazolinone, Methylisothiazolinone.	0.018
Q	dermatologically tested, Nickel Tested, biodegradable surface agents, vegan. Certified as EU Ecolabel Product (reduced environmental impact)	0.006
R	<5% parfum, Benzisothiazolinone, Methylisothiazolinone, non-ionic surface agents, Limonene, Linalool	0.012
S	<5% non-ionic surface agents, Benzisothiazolinone, Methylisothiazolinone, Benzyl Salicylate, Benzyl Alcohol, butylphenyl, Methylpropional, citronellol, hexyl cinnamal, linalool, Polyphosphate	0.025
T	dermatologically tested, Nickel Tested, biodegradable surface agents, vegan. Certified as EU Ecolabel Product (reduced environmental impact)	0.009
U	Surface agents of vegetable origin. Certified as EU Ecolabel Product (reduced environmental impact)	0.020
V	Alcohol, Butyl Glucoside, Sodium Laureth Sulfate, Potassium Cocoate, Caprylyl/Capryl Glucoside, Phenoxyethanol, Parfum, Tetrasodium Glutamate Diacetate, Colorants. Certified as EU Ecolabel Product (reduced environmental impact)	0.005

Table 2 - Average indoor temperature and relative humidity conditions and outdoor O₃ levels during the experimental campaign.

	Indoor temperature (°C)	Indoor RH (%)	Outdoor O ₃ (µg m ⁻³)
Average	26.0	48.6%	117
Standard deviation	0.9	3.9%	15.1

Table 3 - Average EF values for the investigated cleaning products.

Product	EF _{fs} (part. m ⁻²)	EF _{mL} (part. mL _{product} ⁻¹)
A	1.1×10 ¹¹	8.8×10 ¹⁰
B	1.0×10 ¹¹	8.4×10 ¹⁰
C	8.3×10 ¹⁰	6.9×10 ¹⁰
D	9.4×10 ¹⁰	7.9×10 ¹⁰
E	5.6×10 ¹⁰	4.5×10 ¹⁰
F	2.7×10 ¹⁰	2.3×10 ¹⁰
G	2.5×10 ¹⁰	2.1×10 ¹⁰
H	6.4×10 ⁹	5.4×10 ⁹
I	7.2×10 ⁹	7.2×10 ⁹
O	1.5×10 ⁹	1.3×10 ⁹
L, M, N, P, Q, R, S, T, U, V	Non-emitting products	

Figure captions

Figure 1 – Illustrative example of particle number concentration trends measured through the FMPS 3091 during one of the three tests performed for product A (black lines) and product V (red lines) in the chamber: total particle number concentrations for the entire size range (5.6-560 nm, dashed lines) and nucleation mode concentration (8-12 nm size range, solid lines). Data are reported 1-s sampling frequency.

Figure 2 – Illustrative example of particle number distribution evolutions measured through the FMPS 3091 during one of the three tests (corresponding to the concentrations reported in Figure 1) performed for product A (a) and product V (b) in the chamber. Particle size distributions are reported as 1-min average values.

Figure 3 – Illustrative example of contours plots reporting particle number distribution evolutions measured through the FMPS 3091 during one of the three tests (corresponding to the concentrations reported in Figure 1) performed for product A (a) and product V (b) in the chamber. Contours plots of the particle size distributions are reported as 1-min average values.

Figure 4 – Correlation between total particle number concentrations measured through the CPC and the FMPS for the illustrative tests on product A (a) and product V (b) (reported in Figure 1) in the chamber. Data are reported as 1-min average values.

Figure 5 – Particle number concentration trends measured through the FMPS 3091 during the tests performed in the actual indoor environment using product B (black lines) and product N (red lines): total particle number concentrations for the entire size range (5.6-560 nm, dashed lines) and nucleation mode concentration (8-12 nm size range, solid lines). Data are reported 1-min sampling frequency.

Figure 6 - Contours plots reporting particle number distribution evolutions measured through the FMPS 3091 during the tests performed in the actual indoor environment (corresponding to the concentrations reported in Figure 5) using product B and N. Contours plots of the particle size distributions are reported as 1-min average values.