Carbon dioxide snow cleaning of paper

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Abstract
The cleaning of particles from smooth and rough paper surfaces using a high-speed CO2 snow jet was investigated. The measurements included characterization of the jet properties, determination of the cleaning efficiency, and evaluation of any possible adverse effects. The method was compared with nitrogen jet cleaning and dry cleaning by commercial materials. The results showed that the CO2 snow jet is able to effectively remove particles from the paper surface and did not cause any observable degradation. The CO2 snow jet cleaning compared with the mechanical dry cleaning showed similar effectiveness without any adverse effects on the paper surface. It was proved that the CO2 snow technique is a suitable method for cleaning common types of paper materials.

Keywords: CO2 snow jet, Dry ice, Dry cleaning, Co-axial nozzle, Paper

Introduction
Particles suspended in the indoor air cause adverse effects on library and archival collections. Generated by various indoor and outdoor sources, they represent a complex mixture of particles that differ widely in chemical composition and size. Typical indoor sources in libraries and archives are related to activities conducted indoors (such as maintenance or cleaning) and in rooms accessible to public and visitors (skin and clothing abrasion, mineral particles brought on shoes) [1–5]. These processes are the principal sources of coarse particles (> 1 µm) composed mainly of organic and mineral matter. The major source of indoor fine particles (< 1 µm) is the ambient accumulation mode particles (0.1–1 µm), unfiltered indoors through the building envelope [6, 7]. These particles represent the most harmful portion: they consist of elemental carbon (soot) directly emitted from combustion and organic matter, and ammonium sulphate and nitrate formed by gas-to-particle conversion [6, 8–10]. Due to the small size, they infiltrate from ambient air most easily and once indoors they deposit onto all available surfaces, penetrating into books and porous surfaces [11, 12]. Organic matter and ammonium sulphate contribute to chemical degradation of paper, and fine carbonaceous particles cause the soiling of surfaces and absorption of gaseous pollutants [13–15].

To minimise the adverse effects, books and documents should be kept free of dust. The simple technique for removing surface deposits is dry cleaning, which is done using brushes, erasers, and sponges. For documents in good condition, the surface can be lightly dusted with a soft brush in combination with a vacuum cleaner. More stubborn dirt can be removed with a plastic eraser. Surface cleaning sponges can be used for sooty or mouldy deposits [16]. Prior to the cleaning, it should be taken into account that the cleaning treatment can also affect the physical state of documents. Some erasers cause abrasion and leave a detectable amount of eraser material within the fibres of paper and textiles, altering surface colour, brightness and texture. The wrong cleaning technique can also ingrain fine particles deeper into porous paper or fibres of textiles [17–20].

Alternative dry cleaning techniques include surface cleaning using a high-speed air jet, carbon dioxide (CO2) snow or carbon dioxide (dry ice) pellet blasting. Particle detachment is caused by drag force from the high-speed gas flow, enhanced by collision force of fine dry ice
particles formed in jet by expansion of liquid CO₂ or large CO₂ particles mixed into the air flow. Most all of these techniques primarily developed for specific needs of the aerospace and micro-electronics industries are now used in many other applications [21]. Dry ice snow and dry ice blasting have previously been tested in cleaning of some historical artefacts and art objects, particularly to evaluate certain positive characteristics such as the fast and non-aggressive cleaning of some materials, and the ease of waste removal.

Sherman et al. [22] performed tests of CO₂ snow for the removal of particle and hydrocarbon-based contaminants from the surface of different materials (metals, semiconductors, ceramics, glass, polymers) with particular note given to reduction of surface hydrocarbons. The CO₂ snow cleaning measurements were compared with samples which were cleaned using a conventional solvent process. The results showed that the CO₂ snow cleaning is comparable to the solvent cleaning. It was also observed that CO₂ snow removed particles and other debris and therefore it was recommended for other applications.

Shockey [23], in an early application of CO₂ snow on art objects, removed a white haze formed by crystalline deposits on Robert Morris’s Model structure made of cellulose acetate butyrate at the Smithsonian. Odgaard [24] used carbon dioxide snow, generated by the liquid CO₂ technique to clean textiles and basketry. In tests, the samples of basketry and basketry/textiles dusted with artificial dust were cleaned either by brushing, brushing/vacuum cleaning or CO₂ snow. The cleaning efficiency determined by weight was approximately 71–79% for liquid CO₂ and between 44 and 54% for both brushing methods.

Tsang and Babo [25] performed tests of fine soot particle removal, partially embedded in surface of acrylic emulsion paint. In tests the CO₂ snow method was compared with atomic oxygen cleaning and the traditional dry cleaning with different commercial dry cleaning products recommended for smoke-damaged artworks. CO₂ cleaning did not effectively remove soot most probably due to presence of embedded fine particles and caused small impact holes, indicating loss of original matter.

Součková et al. [26] compared CO₂ snow and nitrogen jet cleaning with infrared TEA CO₂ laser cleaning of vegetable tanned calf leather. The results showed that the perceptible damage was observed by the SEM after the nitrogen jet cleaning and increased after the CO₂ snow application. However, the laser cleaning (fluence 0.69 J/cm², pulse duration 100 ns, number of pulses 2–500) removed particles already after irradiation by 2 pulses with the efficiency increasing with the number of pulses but with perceptible degradation that occurred after irradiation of 50 pulses. Dry ice blasting and wiping-and-vacuuming have been used to remove soot from books exposed to smoke [20, 27]. Molen et al. [28] and Cutille and Kim [29] measured the performance and efficiency of dry ice blasting in the removal of coatings from metallic artifacts. The results showed that all techniques are faster than the classical dry cleaning. Dry ice blasting was the most effective in the cleaning of metallic artifacts [28, 29], quite effective in removing soot from canvas, and leather bookbindings [20, 27]. Also, in the above study CO₂ snow cleaning of polymer surfaces was less effective and even caused some damage to surfaces [25]. One study documented damage while cleaning vegetable tanned calf leather [26].

As discovered, these methods proved to be viable but have also some limitations, related to the rapid decrease of the local temperature and the mechanical strength of the jet which can contribute to the surface damage of the more sensitive materials [25]. To minimize the potential damage, the less aggressive cleaning conditions with lower but still acceptable efficiency of particle removal could be used [30]. Therefore, to avoid possible physical damage, tests are needed prior to the application of any of these methods.

In this study, we performed tests of nitrogen high-speed jet and CO₂ snow cleaning of rough (cotton-based) and smooth (wood-based) paper surface, soiled by submicron particles, typical for the naturally ventilated depositories. Cotton paper has been used since the fifteenth century but was replaced by wood pulp paper in the nineteenth century. As a result, cotton cellulose is a typical raw material found in collections of early printed books and wood cellulose is common for modern printed books. Cotton cellulose differs from wood cellulose by having higher degrees of polymerization and crystallinity, which makes cotton paper more stable and resistant to the physical and chemical changes [31].

We also performed tests of the cleaning of paper soiled by typical dust collected in a library and two synthetic dusts composed mainly by mineral dust and/or carbonaceous particles. We then compared the results with traditional dry-cleaning of the same samples. The experimental results were compared with the theoretical calculations of removal and adhesion forces. The purpose was to discover the suitability and conditions for high-speed jet and CO₂ snow cleaning as an alternative method for removal of fine dust particles from the surfaces of books and manuscripts.
**Methodology**

**CO₂ snow jet**
Tests of CO₂ snow cleaning were performed using a Precision Spray Cleaning Pen (SnoPen SP 2000, Clean-logix) [32]. This instrument generates a CO₂ snow cleaning stream of dry ice snow particles supported by a co-axial nitrogen flow at high-velocity. The particles are formed by a flash-atomization of liquid carbon dioxide delivered to the inner nozzle from the pressure cylinder and accelerated by the high-velocity flow of nitrogen from the outer nozzle. The flow rate of nitrogen is controlled independently by injection pressure (0.08–0.50 MPa). The liquid carbon dioxide supply is controlled by a micro metering valve and operates only with the co-axial flow of nitrogen. As stated by the producer, the flow rates of both components are the main factors determining the spray characteristics and by combination of both parameters one can arrange proper cleaning conditions—efficient cleaning and no physical damage of the cleaned object.

The properties of the CO₂ snow jet were characterised. The volume flow rate of nitrogen was measured using a glass rotameter (accuracy of 4%). To determine the mass flow rate of the carbon dioxide, the stream of gases and dry ice particles passed first through a heat exchanger where all particles of CO₂ evaporated. The volumetric flow rate of remaining gaseous mixture was again measured by the rotameter and the flow rate of CO₂ was calculated subtracting the previously measured N₂ flow rate. Every measurement was repeated three times.

The shape of the jet was simultaneously determined using the flow field visualisation by the particle image velocimetry (PIV, Dantec Dynamics, laser Quantronix Darwin Duo 80 W, high-speed camera Photron Fast-cam Mini SX200). In addition, the local impaction pressure was measured by a pressure sensor AP-43 (Keyence corp.) and the temperature of the surface by an infrared thermal-imaging camera (Testo 872) at the impaction point of the jet. Every measurement was repeated three times.

**Paper samples**

**Samples preparation**
Two types of paper (cotton-based and wood-based) were used for tests. The results were subsequently verified using historical paper. The sheets of different types of paper were cut with scissors into 30 × 30 mm samples.

The tests were performed with two samples of paper: Whatman Grade 1 filter paper and Holmen BOOK Cream 2.0 paper. The papers differ in quality innate to the raw materials and manufacturing process. Whatman filter paper is composed of cotton cellulose fibres which cling together forming a porous structure. Holmen paper is made from fresh wood fibres. It is made up of 81–86% mechanical pulp and 7–12% pigments and fillers (chalk and clay). The paper has a smooth surface suitable for printing. The surface structure of both papers is shown in Fig. 1.

The methods were then verified utilizing a sheet of paper stored for approx. 60 years in a depository of the National Archives in Prague (Fig. 2). The type of paper was identified using the phloroglucinol solution by a drop method.

The Whatman paper samples were soiled with various fine particles representing dirt: soot generated by a candle, PM1 ambient particles, and laboratory-generated

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**Fig. 1** Scanning electron micrographs of a Whatman paper and b Holmen paper
monodisperse ammonium sulphate. Soot and PM1 particles were collected using a Leckel LVS-3 sampler (Sven Leckel Ingenieurburo). Monodisperse ammonium sulphate particles were deposited using equipment described in a previous study [33].

In addition, Whatman and Holmen paper samples were soiled with typical dust collected in depositaries of the National Library of the Czech Republic during the cleaning of books with the Depulvera book cleaning machine, as well as with two commercial synthetic dusts: Ashrae 52.1 (Powder Technology Ltd. UK) and Ivory Black 12,000 (Kremer Pigmente GmbH & Co., Germany). The Library Dust is composed mainly of organic matter [6], Ashrae Dust consists of 72% mineral matter, 23% carbon black soot and 5% cotton fibres [34]. The Ivory Black is a black pigment composed of charred ivory and calcium phosphate [35]. The samples were contaminated by the dust using a brush and evenly distributed on the surfaces by a rubber roller. A list of samples is provided in Table 1.

### Analysis

The effects of the treatments were examined microscopically and analysed by the colour, the folding endurance, and the pH of the cold water extract of the paper measured before and after the treatment.

Microscopic analyses were performed using a scanning electron microscope (SEM, Tescan Indusem, samples coated by Au) and a 3D optical microscope (Hirox RH 2000).

Colour change was measured by a photospectrometer (CM-700d, Konica Minolta) four times before and after cleaning each sample and evaluated using the CIE Lab colour space, where $L^*$, $a^*$, and $b^*$ represent black-white,
red-green, and yellow-blue scales, respectively. The colour measurements were performed before and after the treatments and the average differences ($\Delta L^*$, $\Delta a^*$, and $\Delta b^*$) were used to calculate the total colour change ($\Delta E$):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$  \hspace{1cm} (1)

Because the CIELab space is nonuniform the results were compared with the formula $\Delta E_{2000}$ (mathematically expanded) calculated according to Luo et al. [36]. This formula is used especially for determining the colour difference in its assessment of industrial products.

In case of samples artificially soiled by Library Dust, Ashrae Dust, and Ivory Black, only the dominant parameter $L^*$ was used to evaluate the effectiveness ($\eta$) (%):

$$\eta \approx \frac{\Delta L_p - \Delta L_c}{\Delta L_p} \cdot 100$$ \hspace{1cm} (2)

where $\Delta L_p$ are values of $L^*$ measured before after the dust application and $\Delta L_c$ are values of $L^*$ measured before and after the cleaning.

Folding endurance was measured by a twin folder tester (13,505, Schopper—Frank) under a standard tension of 9.81 N as a number of double folds for the machine and cross directions using 10 parallel samples for each direction. Before measuring, the samples were conditioned at a temperature of 23.0 °C and relative humidity 50.0% [37]. Further, the pH value of the cold-water extracts was measured using a pH Meter Orion Star A214 with an Orion 8172BNWP ROSS Sure-Flow pH electrode (Thermo Scientific) using 10 parallel samples.

The efficiency of removal of PM1 and the ammonium sulphate particles was evaluated using sulphate concentration analysed before and after the cleaning by Ion Chromatography (Dionex ICS-5000, Thermo Scientific). The soot samples were analysed gravimetrically by weighing filters before and after exposition, and before and after cleaning using microbalance with ± 1 µg sensitivity (Sartorius M5P, Data Weighing Systems). The analytical procedure is described in detail in the previous study [6]. The measurements were performed using two parallel samples. The cleaning efficiency $\phi$ (−) was approximated by:

$$\phi = 1 - \frac{C_a}{C_b}$$ \hspace{1cm} (3)

where $C_a$ and $C_b$ (µg/cm²) are the mass concentrations of soot and/or sulphate after and before cleaning.

Further, a potential long-term effect of cleaning was tested using accelerated thermal aging at 105 °C for 144 h [38]. The tests were performed for clean and Ivory Black samples of the Holmen paper.

Modelling

The model compared drag and collision forces exerted on adhered particles by the nitrogen jet and the CO₂ snow jet and the van der Waals adhesive force binding the contaminant to the surface. The forces were calculated at conditions the experiments were performed assuming the contaminant removal can occur when removal forces overcome the adhesive force (see Additional file 1).

Results

Characterization of the jet

The effect of flow rates of both components on characteristic features of the CO₂ snow jet (velocity, shape, pressure, temperature) was examined. The co-axial nozzle comprises an inner circular tube with diameter 0.8 mm and an outer annular tube with inner and outer diameter 1.5 mm and 2.0 mm, respectively (Fig. 4).

The results showed that the volume flow rate of nitrogen ranged from 0.3 to 1.4 l/s and increased linearly with the injection pressure (0.08–0.50 MPa). Further, the mass flow of liquid carbon dioxide ranged approximately from 2.5 to 4.0 g/s (minimal and maximal adjustable feeding). The CO₂ snow jet was partially focused with increasing nitrogen flow producing narrower cone spray (Fig. 5a, b), whereas the influence of the CO₂ flow rate was negligible (Fig. 5c, d).

The results also revealed that the local impaction pressure increased with both the volume flow rate of the co-axial nitrogen and the mass flow rate of carbon dioxide (Fig. 6) and that the CO₂ snow jet caused a rapid decrease of the surface temperature (10–20 °C/s) of the cleaned material.
In an additional test, we attempted to discover whether a higher co-axial flow of nitrogen with ambient temperature of approximately 20 °C could compensate the cooling effect of the jet. However, we found that while increasing the flow rate of nitrogen, the cooling rate of the jet could slightly increase as well (Table 2; Fig. 7). The results also showed that after treatment using only the nitrogen jet, the surface temperature change was negligible.

The explanation may be that due to the higher flow rate, fewer of the dry ice particles evaporate in the jet but more upon impaction surface, enhancing the cooling effect [39].

Cleaning of paper
Two criteria were considered when assessing suitability: (a) the method should not cause any damage and (b) it should be sufficiently effective.

Degradation
The first tests were performed to determine the effect of the cleaning conditions on the properties of the less stable Holmen paper. The purpose was to assess any possible surface damage caused by the incident jets. The first set of parallel samples was cleaned by the CO2 snow jet with a carbon dioxide flow rate of 3.0 g/s and a nitrogen flow rate of 1.4 l/s. The second set was treated using only the nitrogen jet at the same flow rate.

The effects of the treatment were examined microscopically and analysed according to the colour change, the folding endurance, and the pH value of the cold-water extract of the paper as measured before and after the treatment. The colour measurements reflect changes of the esthetical value, the folding endurance is sensitive to changes in the structural properties of paper and pH indicates any changes of stability. All of these methods are commonly used for the evaluation of paper conservation interventions [40, 41] and their combination can provide more comprehensive information about paper properties.

The microscopic observation did not show any remarkable changes in the surface structure nor any significant changes of the fibres’ surface. With respect to the minimal change in colour perceptible by humans, defined as ΔE = 1.00 [42], both jets did not cause any visually perceived change of the surface (Table 3). A change in yellowness ≤ 0.5 points after treatment specified as a high optical stability of paper [43] might also indicate negligible effect on optical properties.

The results of the folding endurance tests did not show any effect caused by the nitrogen jet in machine direction folding strength. The CO2 snow jet caused a decrease of about 20% in the machine direction folding strength. Both jets also caused a decrease of about 20% in the cross direction folding strength (Table 4). With respect to known high scatter in measurements of the folding endurance [31] and a loss of fold endurance ≤ 50% after accelerated aging specified as high strength stability of printing and writing paper [44], the jet cleaning caused insignificant changes of structure.

The tests of pH value of the cold-water extracts revealed that the average pH value of 7.8 measured before the treatment remained practically unchanged, with only a small increase of approximately 1.4% after

### Table 2 Change of the minimal surface temperature of paper before and after the treatment by the CO2 snow jet with the carbon dioxide flow rate 3.0 g/s and different nitrogen flow rates

| N2 flow rate (l/s) | Whatman (°C) | Holmen (°C) |
|-------------------|-------------|-------------|
| 0.3               | −30.6 ± (1.9) | −31.0 ± (1.5) |
| 0.6               | −32.0 ± (1.8) | −32.9 ± (1.1) |
| 1.4               | −34.6 ± (2.3) | −36.7 ± (2.2) |
the application of the nitrogen jet and of approximately 2.8% after the CO2 snow jet treatment.

As found, both jet cleaning techniques did not cause any significant alteration of the examined properties and/or any observable changes of surface structure. With respect to the low resistant form of cellulose used in the test, the snow jet can be safely used for cleaning of surfaces of common types of pure cellulose paper.

**Effectiveness**

The efficiency of the fine particles removal was examined using three types of particles deposited on the Whatman paper (PM1, ammonium sulphate, and soot). The average mode size of the PM1 fraction reported by Mašková et al. [7] was 0.3 µm with the geometric standard deviation (GSD) of 1.83. Laboratory generated ammonium sulphate and soot had modes of the mass concentration at 0.2 and 0.12 µm with the GSD of 1.29 and 1.68, respectively. The samples were cleaned by the nitrogen jet and by the CO2 snow jet with nitrogen flow rates of 0.3, 0.6, and 1.4 l/s and the constant flow rate of carbon dioxide of 3.0 g/s.

Figure 8 shows the cleaning efficiency as a parameter of the nitrogen flow rate. The nitrogen jet alone was almost inefficient in the removal of the submicron-sized particles. When adding the dry ice cleaning, submicron-sized particles were removed with a removal

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**Table 3** Colour change of the Holmen paper caused by the nitrogen jet and the CO2 snow jet (± SD)

|        | ΔL*   | Δa*   | Δb*   | ΔE    | ΔE2000 |
|--------|-------|-------|-------|-------|--------|
| N2 jet | − 0.10 (± 0.37) | 0.00 (± 0.15) | 0.11 (± 0.28) | 0.50 (± 0.15) | 0.35 (± 0.15) |
| CO2 snow jet | − 0.34 (± 0.23) | 0.12 (± 0.08) | 0.19 (± 0.21) | 0.43 (± 0.18) | 0.37 (± 0.12) |

**Table 4** Folding endurance of the Holmen paper treated by the nitrogen jet and the CO2 snow jet

|         | No treatment | N2 jet | CO2 snow jet |
|---------|--------------|--------|--------------|
| Machine direction | 54.9 (± 14.0) | 54.8 (± 13.5) | 45.7 (± 9.7) |
| Cross direction  | 4.2 (± 0.4)  | 3.3 (± 0.7)  | 3.4 (± 0.8)  |
efficiency quickly rising with an increase in the nitrogen flow rate.

The surface of samples was also examined by the SEM microscope. The results showed that the CO₂ snow jet can also remove particles ingrained into the surface. An example of soot particle removal using the nitrogen jet and the CO₂ snow jet is shown in Fig. 9.

Comparison of the jet and mechanical dry cleaning methods

The last phase tests were conducted to compare the effectiveness of the both jet-cleaning methods with the classical dry-cleaning performed with commercial materials. The experiments used samples of the Whatman and Holmen papers, contaminated by dust collected in library depositories and two commercial synthetic dusts Ashrae Dust and Ivory Black.

As found from the observations samples with the Library Dust were cleaned most easily, cleaning of samples with the Ivory Black was more difficult, and the Ashrae Dust was the most resistant. The cleaning of the Holmen paper was overall more efficient than the cleaning of the Whatman paper. The results also revealed that both techniques did not cause any alteration of the surface. The examples of the CO₂ snow cleaning of the Whatman paper contaminated by the Ashrae Dust and by the Ivory Black are shown in Fig. 10.

The results were evaluated by visual observation, optical and SEM microscopes, and by measuring the colour change. The colour measurement showed that the most efficient was the Groom/Sticker eraser, followed by the Faber Castell, and less efficient were the Wallmaster and Wishab sponges. Further, the Library Dust was removed most easily, the cleaning of samples with the Ivory Black was more difficult with a tendency to smear and the Ashrae Dust was the most resistant. The SEM examination showed that all materials caused some damage to the Holmen paper with visible crumbs of the Wishab eraser remaining (Fig. 11b), released fibres (Fig. 11a, c, d) and even changes of fibres surface after the Faber Castell application (Fig. 11d). In contrast, neither jet caused any alteration of the Holmen paper surface (Fig. 11e, f). It was also found that the mechanical cleaning could not remove contaminant particles embedded in the paper’s surface and even led to the ingraining of some powder into the fibrous structure.
The effectiveness of each cleaning method was characterised by the total colour change ($\Delta E$). Due to minor changes of $a^*$ and $b^*$, parameter $L^*$ was used to evaluate the effectiveness ($\eta$) (%). The results are shown in Table 5.

As can be seen, the efficiency of different cleaning methods is comparable. It could be explained that most of the darkening is caused by the larger particles, which are most easily removed by any cleaning technique. This would also correspond to the higher efficiency of cleaning of smooth surface of the Holmen paper. As can be seen from Fig. 12 the lower efficiencies coincide with the observed alteration of the surface, such as smearing of impurities or residues of cleaning material left on the surface (e.g., Fig. 12a). Further, changes of the surface structure can be seen after the Faber Castell application (Fig. 12d). The CO$_2$ snow jet cleaning was effective in the lower layers of the paper surface, including interfiber spaces (Fig. 12f), whereas the nitrogen jet had lower efficiency (Fig. 12e). The mechanical cleaning methods were not effective at the lower fibers and interfiber spaces (Fig. 12a–d).

Possible long-term effects of cleaning were assessed using accelerated thermal aging of Ivory Black and clean samples. The effects of the aging were examined microscopically and analysed according to the colour change, the folding endurance, and the pH value of the cold-water extract of the paper.

The SEM analyse did not showed any substantial changes of the surface morphology after the aging. The colour change measurements revealed mainly darkening and yellowing of the Holmen paper (Table 6). However, the results of cleaned samples and reference were comparable. The colour change of the Watman paper was negligible. The folding endurance and pH value remained practically unchanged. Although the results did not show any substantial changes of paper properties after the accelerated aging, the potential risk of degradation caused by remains of the cleaning material should be considered.

**Model**
This study examined the removal via CO$_2$ snow and nitrogen jets of contaminant particles deposited on paper surfaces. The purpose was to find out if these techniques could be used for cleaning of surfaces of historical documents contaminated by fine dust. Both methods were
tested experimentally evaluating the efficiency of fine particle removal and no evident damage to the surface as criteria. In order to assess the suitable operating conditions, the experimental results were compared with the theoretical calculations of removal and adhesion forces at the moment of separation. This included the van der Waals force as the force of adhesion, and the Stokes drag force and the impact force due to collision with the dry ice particles as the removal forces. The calculations were performed for PM1 (0.1–1 µm), monodispersed ammonium sulphate (0.2 µm) and soot (0.1 µm) contaminant particles, and dry ice particles ranging from 0.2 µm to 6 µm, considering geometric restriction for particles impacting at angle $45^\circ \leq D_{\text{imp}} \leq 5.82 D_{\text{dep}}$. The dry ice particles with sizes 0.5–11 µm produced by expanding liquid carbon dioxide were measured by Lin et al. [46].

Table 5  Effectiveness ($\eta$) of different cleaning methods in % (± SD)

|                  | Wallmaster | Wishab | Groom/Stick | Faber Castell | $N_2$ jet | $CO_2$ snow jet |
|------------------|------------|--------|-------------|---------------|-----------|-----------------|
| **Ashrae Dust**  |            |        |             |               |           |                 |
| Whatman          | 14 (± 3)   | 33 (± 7)| 37 (± 8)    | 75 (± 16)     | 34 (± 7)  | 38 (± 8)        |
| Holmen           | 62 (± 13)  | 68 (± 14)| 95 (± 17)  | 78 (± 15)     | 52 (± 11) | 82 (± 15)       |
| **Ivory Black**  |            |        |             |               |           |                 |
| Whatman          | 52 (± 3)   | 17 (± 2)| 97 (± 7)    | 94 (± 7)      | 47 (± 4)  | 56 (± 4)        |
| Holmen           | 59 (± 4)   | 80 (± 4)| 92 (± 5)    | 92 (± 6)      | 68 (± 5)  | 88 (± 6)        |
| **Library Dust** |            |        |             |               |           |                 |
| Whatman          | 100 (± 28) | 94 (± 27)| 93 (± 26)  | 76 (± 24)     | 22 (± 7)  | 55 (± 18)       |
| Holmen           | 75 (± 25)  | 79 (± 25)| 75 (± 23)  | 87 (± 24)     | 57 (± 19) | 54 (± 17)       |

Fig. 11  Example of the Holmen paper contaminated by the Ashrae Dust cleaned by a Wallmaster, b Wishab, c Groom/Stick, d Faber Castell, e nitrogen jet, and f $CO_2$ snow jet (see the clean Holmen paper in Fig. 1)
the size 0.2 µm was considered assuming dry ice particles can also evaporate.

**The nitrogen jet particle removal**

There are two main forces considered in the aerodynamic cleaning the van der Waals adhesion force binding particles to a surface, and the Stokes drag force caused by the gas flow which acts as the removal force. The van der Waals force is proportional to the contaminant particle diameter $d$, while the Stokes drag force is proportional to the $\sim d^2$ [47] and hence decreases more rapidly as the contaminant particle becomes smaller. As a result, the Stokes drag is insufficient in the submicron-size particles removal (Fig. 14). This conclusion agrees quite well with the results of submicron particle cleaning which were almost ineffective (Fig. 9).

Moreover, Fig. 13 also revealed that for coarse particles, the drag forces can overcome the adhesion forces. This corresponds well with results of coarse particles cleaning (Ashrae Dust, Ivory Black, and Library Dust) which showed comparable efficiencies for both the nitrogen and the CO$_2$ snow jets (Table 4) indicating that the drag force

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**Table 6** Colour change of the Holmen paper caused by the accelerated aging (± SD)

|                | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta E^*$ | $\Delta E_{2000}$ |
|----------------|-------------|-------------|-------------|-------------|------------------|
| Wallmaster     | 3.88 (± 0.14) | -1.53 (± 0.08) | 0.55 (± 0.06) | 4.21 (± 0.15) | 2.69 (± 0.14) |
| Wishab         | 3.88 (± 0.20) | -1.37 (± 0.21) | 0.50 (± 0.06) | 4.15 (± 0.24) | 2.63 (± 0.21) |
| Groom/Stick    | 3.88 (± 0.15) | -1.52 (± 0.13) | 0.59 (± 0.07) | 4.21 (± 0.15) | 2.69 (± 0.15) |
| Faber Castell  | 3.81 (± 0.14) | -1.49 (± 0.14) | 0.57 (± 0.08) | 4.14 (± 0.14) | 2.65 (± 0.15) |
| Nitrogen jet   | 3.69 (± 0.19) | -1.64 (± 0.22) | 0.67 (± 0.07) | 4.10 (± 0.15) | 2.68 (± 0.17) |
| CO$_2$ snow jet| 3.87 (± 0.15) | -1.74 (± 0.16) | 0.71 (± 0.09) | 4.30 (± 0.13) | 2.83 (± 0.15) |
| Reference      | 3.95 (± 0.10) | -1.62 (± 0.11) | 0.70 (± 0.08) | 4.33 (± 0.12) | 2.85 (± 0.13) |
can cause particle removal. Silicon dioxide (size fraction 5–80 µm) was used for modelling, because it represents approx. 70% of the Ashrae Dust [34].

The CO₂ snow jet particle removal
Figure 14a, b shows conditions modelled for the mode-sizes of PM1 and ammonium sulphate particles. As these particles were mostly irregular, we utilized the impact sliding mechanism: the contaminant particle will be removed if the ratio of forces $r^*$ is higher than 1 (see Additional file 1). The results revealed that the cleaning efficiency grows with the nitrogen flow rate and that PM1 particles can be at least partially removed under all tested operation conditions. For the sulphate particles the flow rate of 0.3 l/s is ineffective, whereas, 0.6 l/s can partially remove contaminants, and 1.4 l/s has even higher cleaning efficiency. These findings correspond well with results of submicron-size particle cleaning experiments (Fig. 8).

Finally, it is important to bear in mind that the experiments performed with nitrogen and dry ice jet cleaning of paper surfaces were evaluated using the simple theoretical calculation of adhesion and removal forces in order to delineate the processes involved. Certainly, the modelled situations differ from real conditions (e.g., assuming only spherical particles deposited on flat smooth surface compared to irregular particles deposited on and into fibrous surface and many other simplifications) and there are many different parameters that affect the flow-driven particle removal [48] that should be considered. Nevertheless, these findings could help to better understand the principles of both methods and to attain further knowledge for application.

Cleaning of archival paper
The methods were verified using the cleaning of archival paper. The sheet was identified as a wood-based paper. Microscopic investigation and colour change analysis of the paper surface were performed before and after cleaning. The microscopic examination did show any significant changes in the surface structure (Fig. 15). The analyses also revealed negligible removal efficiency of the nitrogen jet, whereas after the CO₂ snow jet cleaning the amount of contaminant particles was significantly reduced.

The total colour difference ($ΔE$) after nitrogen jet and CO₂ snow jet treatment was 0.52 and 6.18, respectively. This shows the negligible effect of the nitrogen jet, which is not perceptible by an observer ($ΔE < 1.00$). For comparison $ΔE2000$ after nitrogen jet and CO₂ snow jet treatment was 0.36 and 5.30, respectively. However, after the CO₂ snow jet cleaning, the difference exceeded the limit $ΔE = 5.00$ which indicates that an...
observer could notice two different colours [42]. This corresponds well with the results of test samples cleaning and modelling. However, particular materials which are partially damaged or degraded require individual evaluation and preliminary tests before the treatment.

Conclusions
The removal via the CO₂ snow jet and the nitrogen jet of dust particles deposited on paper surface has been investigated. The measurements included characterization of the CO₂ snow jet properties, examination of the possible adverse effects and evaluation of the cleaning effectiveness. The results were compared with the nitrogen jet cleaning and the dry cleaning by commercial cleaning materials. Based on results the following conclusions are drawn:

- The CO₂ snow jet cleaning is effective in the removal of particles from paper surfaces including the submicron-sized particles ingrained in the surface.
- This method has not caused any observable damage of surface and any substantial change of mechanical and optical properties of mechanical pulp paper.
- The CO₂ snow jet has been generated by the expansion of liquid carbon dioxide using a co-axial nozzle which supported the flow of nitrogen. The jet properties and hence the effectiveness of cleaning could be easily controlled by altering the nitrogen flow rate.
- The results of the CO₂ snow cleaning compared with the mechanical dry cleaning showed similar effectiveness without any adverse effects on the paper surface.
- The CO₂ snow technique is suitable for the cleaning of common types of paper materials.

Finally, it should be mentioned that there are also other properties that were not examined but should be considered: the CO₂ snow cleaning is fast (comparable or faster than traditional dry cleaning methods), it does not produce any residue except for the removed contaminants, it can be used for cleaning small samples, it could be used also for the cleaning of less accessible surfaces e.g. inside headband or at joint area of books), and the equipment does not need much space. On the other hand, an initial investment to the CO₂ snow jet is essential (in the order of thousands of Euro). However, the operating costs are relatively low and cover mostly only the CO₂ and the carrier gas consumption.

Supplementary Information
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Additional file 1: Table S1. List of material properties used for modelling.

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Authors’ contributions
LM performed the nitrogen jet and CO₂ snow jet cleaning, characterised the jets properties, and was a major contributor in writing the manuscript. JS supervised the measurements and was a major contributor in writing the manuscript. PV supervised the samples preparation and the analysis. JN analysed the paper microscopically, by the colour, the folding endurance, and the pH value of the cold-water extract, and supervised the samples preparation. MS cooperated in the samples preparation and the analysis. DN cooperated in the samples preparation and the analysis. VJ performed the SEM analysis. JO cooperated in the cleaning. LO cooperated in the cleaning. TK cooperated in the samples preparation and the analysis. KK cooperated in the samples preparation and the analysis. PS performed the PIV analysis. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

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