The role of SVOCs in the initial film formation and soiling of unvarnished paintings

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Abstract

In recent years increased research efforts and environmental improvements have been directed towards the preventive conservation of the monumental, unvarnished oil paintings on canvas (1909–1916) by Edvard Munch (1863–1944) housed in the University of Oslo Aula. Surface soiling of the paintings has been a documented issue since their display, and the modern-day effect of air-borne particulates and gases on the painting surfaces remains hitherto undocumented. For the first time in the Aula, this study has measured the in-situ time-dependent mass deposit of air pollution onto vertical surfaces over the period of one year (2021–2022). Concomitant measurements of the concentrations of ozone (O_3) and nitrogen dioxide (NO_2) were also taken, to complement periodic data from 2020. The mass deposit was measured through incremental weight changes of Teflon membrane filters, and quartz filters for analysis of elemental/organic carbon (EC/OC), whilst the gaseous pollutants were measured using passive gas samplers. Indoor-to-outdoor ratios (I/O) for O_3 were noted to be higher than those suggested by earlier data, whereas NO_2 I/O ratios were found to be lower, indicating a stronger oxidising atmosphere in the Aula. Just over half of the deposited mass on the quartz filters was found to be OC, with no EC detected. Surprisingly, an overall decrease in the mass deposit from three to twelve months was measured on the Teflon membrane filters. It was hypothesised, based on models reported in the literature, that the source of the OC on the filters was mainly gaseous, semi-volatile organic compounds (SVOCs), which were present in an adsorption/desorption equilibrium that was dependent on possible SVOC emission episodes, relative humidity levels, gaseous oxidative reactions and the particulate matter deposit. A simple mathematical model is proposed to rationalise the observed mass deposits on the filters, together with a discussion of uncertainties affecting the measurements. The hypothesis preliminarily indicates the possible and previously unconsidered role of SVOCs on the initial film formation of soiling layers on the Aula paintings, and could bear implications for their monitoring in the preventive care of unvarnished oil paintings on canvas.

Keywords Indoor air pollution deposit, Organic surface film, Mathematical modelling, Unvarnished paintings, Preventive conservation

Introduction

The monumental oil paintings on canvas by Edvard Munch (1863–1944) have embellished the University of Oslo (UiO) Aula in Norway since 1916. They are unique for being Munch's only monumental public commission that remains in situ. As such they provide solemnity to ceremonies and arrangements in the listed room. Notably, the paintings are unvarnished, with a variety of lean, pastose, and underbound applications that are vulnerable to atmospheric agents, soiling accumulation, saponification, flaking and paint

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loss. They have been subjected to repeated historical surface cleaning [1–3]. Considerable efforts have been made over the past two decades to improve the indoor environment of the paintings, structurally conserve them, and improve the surface presentation [4, 5]. Vulnerable canvas paintings can be protected in microclimate frames [6, 7]. This is, however, difficult or impossible with monumental paintings, like those in the Aula. The vast expanse of painted surface for each Aula painting would imply that glare from any glass covering would somewhat prevent the proper appreciation of the artworks. Furthermore, should so much glass be introduced into the Aula, the acoustics of the room (a property that lends to the listed status of the building) would be invariably modified.

The damage of paintings from air pollution and possible mitigation have been the subject of several studies. Surface soiling from deposition of particles seems usually to be the main concern [8, 9], but damage from gaseous pollutants cannot be excluded [10–14]. The establishment of thin films of semi-volatile organic compounds (SVOCs) on indoor surface has been investigated [15] and discussed [16]. Their possible impact on paintings seems to have been less studied.

Research aim

The aim of the investigations was to measure the annual time-dependent total mass deposits, and the elemental (EC) and organic (OC) carbonaceous mass deposits, from the air to a vertical surface in the UiO Aula, with the intention to simulate the deposits on the monumental paintings' surfaces. The measurements would provide more information on, and contribute to, the development of an improved hypothesis about the initial phases of developing mass deposits and soiling of the cleaned paintings. The hypothesis testing was made possible by some suggested adjustments in this work of a model for the growth of organic films on indoor surfaces, which was provided by Weschler and Nazaroff [16] as a Additional file 1.

A secondary aim was to obtain, for the first time, values of the annual indoor concentration in the Aula of the major deteriorating air pollutants originating from outdoors, nitrogen dioxide (NO_2) and ozone (O_3). The values of the pollutants would be compared with previous assessments based on partial monthly or periodic data, concentration values from the nearby old National Gallery, and from different indoor locations in Oslo [5]. This would allow a reassessment of previous modelling results [5] of the indoor deposits of these air pollutants onto the paintings.

Notable measures against air pollutant deterioration on the Aula paintings

Recent conservation efforts in the Aula have targeted both particulate matter/soiling and gaseous pollutants. The latest condition assessments of the paintings' surfaces were performed in 2022, building on assessments made in 2018, when they were also superficially dusted. Prior to that, the artworks' surfaces were dry cleaned as part of the Munch Aula Paintings (MAP) project refurbishment during 2009–2011. The refurbishment concurrently involved a major renovation of the building envelope [3]. The focus was on the control of the indoor climate to minimise transport of air pollution into the Aula and to the paintings. A ventilation system with particle filtration had been installed in c.1975. During the MAP renovation campaign, the ventilation system was replaced in an attempt to improve the indoor climate. The heating system was changed from wall radiators to heating through the walls from surrounding rooms, and underfloor heating. The marouflaged paintings were insulated from the brick walls behind them. A sluice was designed in the cloak room to reduce dust intake from visitors. These efforts have considerably reduced the damaging atmospheric influences, in particular, the visible soiling rate of the paintings. The Aula is, however, used for many different arrangements. It is intermittently open to the public. Thus, even as the filtration of the air in the mechanical ventilation system probably removes more than 80% of small particles less than 2.5 μm in diameter ($PM_{2.5}$) [5], there is an influx of detrimental air pollution by an undetermined fraction of ventilation through the doors and building shell. The Aula undergoes regular housekeeping, with vacuum cleaning, wet floor cleaning, and floor waxing, which involves the use of products containing SVOCs. Although the rate of soiling has been reduced, as compared to before the renovation of 2009–2011, a need for future surface cleaning of the paintings is still expected [17, 18].

In addition, gaseous air pollutants from outdoors contribute to the paintings' deterioration [12, 14, 19, 20]. Historically, sulphur dioxide (SO_2) was a major acidic deterioration agent. SO_2 concentrations are nowadays very low in Oslo [21, 22], and are expected to be c. 0 μg m^{-3} in the Aula. The major pollutants of concern from outdoors are oxidising ozone (O_3), and the oxidising and acidic nitrogen oxides (NO_x). These gases are known to degrade cultural heritage and artists' materials including varnishes, colorants, and various other organic materials [23]. Their deposition amounts to the surfaces of Munch's paintings has been estimated [5]. Their reactions on the complex surfaces are however mainly unknown. They can be expected to involve, besides the painting materials themselves: adsorbed organic molecules, the

soiling, and water/moisture content [24], and could possibly play a role in accelerating the long-term deterioration of the paintings. For example, it has been suspected that air pollutants might take part in observed zinc soap formation [2, 25]. The campaign reported in this work was performed as a minor research track within a Marie Skłodowska-Curie doctoral fellowship (see Funding). It could be considered a pre-screening and information gathering campaign for the possible later design of more detailed measurements of the soiling deposition, and studies of the concomitant effect of gaseous pollutants.

Materials and methods

In situ deposit monitoring and outdoor pollution gases

Teflon membrane and quartz filters were mounted in situ for passive sampling of air pollution deposits throughout one year (26th March 2021–22nd April 2022) in the Aula. The samplers were mounted onto a thin, stiff, acid-free cardboard plate. This was fastened vertically with frame hanging wire, c. 6.0 m above ground level on the outside of the marble balustrade of the Aula gallery. The mounting was in the approximate central vertical position of the monumental painting surfaces on the neighbouring walls. This was the only location where mounting at this height was practically and aesthetically possible.

Twelve Merck Millipore Fluoropore FSLW 04700 3.0 µm PTFE (Teflon) membrane filters of diameter 47 mm were fixed in cut-out slots, and two GE-Healthcare Whatman quartz filters of diameter 47 mm mounted in Sun Laboratory Model 5 OC/EC Lab Instrument holders were fixed in cut-out circles on the cardboard plate (Fig. 1A). The Teflon membrane filters were mounted with the membranes towards the air, arranged in triplicates (4×3) for demounting every three months. The two quartz filters were mounted with the shallow (c. 1 mm deep) edge of the holder towards the air. They were positioned besides each other below the Teflon membrane filters, for demounting after twelve months.

Passive single or duplicate samplers of NO_2 and single samplers of O_3 of the IVL badge type [26, 27] were mounted under the balustrade besides the cardboard plate. Sampling lasted for periods of one to three months throughout the year (Fig. 1). The gas samplers were mounted with the diffusion barrier nets over their openings facing downwards, to avoid dust deposition on them. The outdoor concentration value of NO_2 and O_3 during the filter exposures were obtained as 24-h averages from the air quality monitoring station in Sofienbergparken, Oslo [28]. This was located 2 km away from the University Aula in the city centre of Oslo in a similar urban background situation.

Fig. 1 The mounting of Teflon membrane and quartz filters on the cardboard plate (**A**), the vertical exposure of the filters, and exposure of the passive gas samplers (also seen in the enlargement) under the Aula gallery balustrade (**B**), and the view towards the paintings in the Aula from the gallery (**C**) in 1955, when grid-like thermal soiling deposits over the stretchers of the paintings on the left and right could be observed. The present room arrangement of the Aula is close to that in the photograph. **C** reproduced with permission from the UiO Universitetshistorisk fotobase

Weighing and observation of filters

All the Teflon membrane filters, and the quartz filters, were weighed before mounting on the cardboard plate at the UiO archaeology laboratory on a Sartorius CPA225D balance with a resolution of 10 µg and variance of 12 ± 9 µg.[1] Three Teflon membrane filters were demounted each time after three, six, nine, and finally twelve months, when the quartz filters were also demounted.

During the demounting in the Aula, the Teflon membrane filters were taken off the cardboard plate and put

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[1] The variance being the average and sample standard deviation (±), of the sample standard deviations of three initial masses of each of the twelve single Teflon membrane filters.

into closed glass Petri dishes. The Petri dishes were kept in a closed polystyrene box in the archaeology laboratory for one week. The box and dishes were then opened, and the filters weighed on an OHAUS Explorer Semimicro balance that had become available, with a resolution of 10 μg and a recorded exposed sample variance of 20 ± 16 μg (calculated as described above for the initial mass recordings). After the weighing the Teflon membrane filters were put back in the Petri dishes and polystyrene box for closed storage.

Six weeks after the last regular sample weighing at the twelfth month, all the Teflon membrane filters were reweighed in the UiO archaeology laboratory on the Sartorius CPA225D balance that was used for the first weighing of all the samples. This was to provide a control of the initially recorded final mass measurements by the OHAUS balance. After the reweighing, the samples were immediately again transferred back to the Petri dishes and polystyrene box for closed storage. In June 2023, the presence of particles on the Teflon membrane filters was investigated by optical microscopy.

The two quartz filters and holders were demounted into polyethylene zipper bags in the Aula. They were immediately transferred to the NILU laboratory and weighed on a Mettler Toledo XP6 balance, with a resolution of 1 μg and variance reported from the manufacturer of 2 μg. They were then analysed for their EC/OC content on a Sun laboratory Model 5 OC/EC Lab Instrument [29, 30]. The carbonate carbon (CC) was not measured separately. Any CC would be included, and is reported below, with the OC. No microscopy observations were made of the quartz filters. The chance for contamination of the filters by, for example, dust during their manipulation, was minimised by the immediate transfer to the storage boxes in each step of the manipulation. It is a possibility that could, however, not be totally excluded. The calculations were made in Excel, and included a one-sided t-test in Xlstat for the significance of the difference of the means of the mass additions of the triplicate samples.

Uncertainties due to balances and RH

Due to the COVID19 regulations in force during the whole exposure period, the filter weighing locations were not openly accessible as foreseen. The NILU ISO certified laboratory with customised, humidity-controlled weighing according to standards [31] was not externally accessible, and could not be used as planned, except at the very end of the experiments. Resultantly, weighing had to be carried out on different available balances at the UiO archaeology laboratory, without standardised humidity control. To reduce uncertainty, a re-weighing of the Teflon membrane filters was carried out once the experiment ended. In addition, a direct comparison of the UiO

Sartorius balance with the NILU high-resolution Mettler Toledo balance was carried out after the regular final mass measurements. This was done by the weighing of calibration standard weights when the laboratories were open again. As a result, the recorded deposited masses on the quartz and Teflon membrane filters were adjusted with a value of $+2.1$ μg cm^{-2}. The difference between the balances was assumed to be due to an incorrect, excessive mass recording by the UiO Sartorius balance compared to the certified NILU Mettler Toledo balance. A similar difference of lower, more correct mass recordings by the OHAUS balance was expected. It was however not possible to directly make this comparison.

Furthermore, the mass changes of both the Teflon membrane and quartz filters may have been influenced by the different air humidity in the Aula, and in the UiO and NILU laboratories during the exposures and weighing. The possible effect of humidity differences between the laboratories was evaluated from the recorded relative humidity (RH) during the weighing (Table 1).

Continuous values of the RH from measurements in the Aula were unfortunately not available for the period of the filter exposures. The RH is however expected to have a typical annual variation, and has been measured in several different periods. The typical RH variations are of a drier winter, and more humid summer and autumn. By combining available periods of data for the same dates and hours as the filter exposures, but from the years 2014 to 2016, a near complete data series of the typical annual RH was obtained. For the period between 19th December and 30th January no data were available, and the RH was simply calculated as the constant average of the near equal start and end RH values of this period. A further assessment of the annual trend in the indoor RH was made by estimating the indoor RH during the periods of these measurements, from 2014 to 2016, from the absolute outdoor humidity (AH), calculated from the RH and temperature (T) values obtained from the nearest meteorological station in Oslo, Blindern [32], by the equation from Camuffo [33]. The calculation was made for the near constant controlled indoor T in the Aula, of 20 °C. The Blindern station is located 3 km north-northwest, and at an elevation 90 m higher than the Aula, which is located 7 m above sea level. The RH and T at the Blindern station was expected to represent the situation outdoors at the Aula well. The indoor RH in the exposure period in 2021–2022 was then estimated from the outdoor AH, calculated from the RH and T in this period, and additionally adjusted by the measured correlation between the indoor measured and estimated RH values from 2014 to 2016. This alternative annual RH series from 2021–2022 was very similar to the measurements from 2014–2016, and resulted in only small differences in the modelling. The estimation of, and modelling from, this alternative annual RH series,

Table 1 Filter and sampler exposure and laboratory relative humidity (RH) and temperature (T) at weighing

	Replicates (no.)	Periods (no.)	Exposure duration (months)	Exposure dates[a]	Laboratory RH(%), T(°C)
Teflon membrane filters	3	4	c. 3	1. 26.03.2021 2. 30.06.2021 3. 01.10.2021 4. 14.01.2022 5a. 22.04.2022 5b. 01.06.2022	1. 40, 20 2. 45, 22 3. 39, 19 4. 38,20 5a. 41, 21 5b. 47, 20
Quartz filters	2	1	c.12	1. 26.03.2021 2. 22.04.2022	1. 40, 20 2. 47, 20
NO$_2$ passive gas samplers[b]	1[c]	6	c. 1 and 3	26.03.2021–22.04.2022[b]	N/A
O$_3$ passive gas samplers[b]	1	5	c. 1.5 and 3		

n/A not applicable

[a] 1: experiment start; 2–5: demounting; 5a: final weighing, 5b: reweighing

[b] See Fig. 3 (*x*-axis) for the mounting/demounting dates through the year

[c] Duplicate samplers in first period

throughout 2021–2022, is provided in Additional file 4. The importance of the uncertainties related to the different balances and the humidity are considered in the discussion of the results ("Results" section) and hypothesis development ("Discussion" section).

Passive gas samplers

The passive gas samplers were brought to and from the Aula in small, closed plastic boxes (Fig. 1). After exposure, the NILU laboratories performed NO$_2$ analysis, by photometry, whereas IVL-Sweden carried out O$_3$ analysis, by ion chromatography.

The detection limit of the O$_3$ sampling was reported from IVL to be 1–1.5 μg m^{-3} for one to three month's sampling, and the measurement uncertainty of one month's sampling was reported to be 10%. The detection limit of the monthly NO$_2$ sampling was reported from the NILU laboratory to be less than 0.1 μg m^{-3}. The precision of the NO$_2$ sampling has been reported to be 5%, and the accuracy, 20% [16, 34].

Mathematical model

The hypothesis developed below in the discussion ("Discussion" section) was tested by the following adjustment of the mathematical model in the literature [16], which provided expressions for mass deposits on the Teflon membrane filters due to SVOC adsorption. The adjustments involved a change in the expressions of the octanol partition coefficients,[2] [35], from constant values to (i) being dependent on the time since the exposure start,

and the RH in the Aula (Eqs. 1, 2 and 3), and (ii) including also a potential SVOC emission episode (Eq. 4). As the gas-phase concentrations of the sorbing SVOCs depend on the partition coefficients, these then also changed over time in the adjusted model. The adjustments were made in the most simplified form that could illustrate the hypothesis, and were not formulated to be exact, nor to describe in detail these combined and quite complex mechanisms. This is since the experimental evidence was not sufficient to distinguish between the described simplified processes, nor to provide chemically/experimentally unique values of their reaction constants by the model fitting.

In the original model, provided by Weschler and Nazaroff [16], the octanol–air partition coefficient of SVOCs to smooth, impermeable surfaces (K_{oa}) was approximated by division into five groups of increasing molecular weight, of [SVOC]$_{1-5}$ with $K_{oa}1$ to $K_{oa}5$. For this experiment with the Teflon membrane filters, the SVOC filter-air partition coefficient is termed, K_s, such that $K_s n = K_{oa} n$ at the start of exposure ($t = 0$). It is assumed that the presence of moisture on the relatively hydrophobic, clean Teflon membrane filters at the start of the exposures (t = 0) was much less than one monolayer, and probably c. 0 nm. It is then hypothesised that both the increasing particle deposit, and (mainly) oxidising reactions of the SVOCs on the surface

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[2] There is a long tradition in environmental chemistry of using the solvent octan-1-ol as a surrogate for a large variety of organic matter when seeking to predict the phase distribution of organic compounds. The octanol–air partitioning ratio (or partition coefficient), K$_{oa}$, is widely used when studying the partitioning of organic compounds between organic matter and

Footnote 2 (continued)

the gas phase. The modelling assumed16 that (i) "the partition coefficient of each SVOC can be approximated by its octanol–air partition coefficient (K$_{oa}$), (ii) that octanol is a reasonable surrogate for the mix of organics that constitute the film, which would include a substantial proportion of oxidized compounds, and (iii) that the surface film exhibits sorptive properties that are adequately approximated by bulk liquid octanol, even when the film is too thin to possess exactly the same thermodynamic properties as a bulk liquid".

by principally O_3, reduced the hydrophobicity of the surface over time. This in turn, in dependence on the RH, increased the surface coverage of adsorbed water, θ_w, on the filters. The average values of the partition coefficients of the SVOCs to the filter surfaces were then proportional to the diminished "dry" filter surface area:

$$K_s n = K_{oa} n \cdot (1 - \theta_w) \tag{1}$$

The moisture on the Teflon surfaces in this expression was simulated by the basic Langmuir isotherm [36]. It described then the surface coverage of water up to one monolayer depending on the air humidity, $\theta_{w,RH}$, that was represented in the model by the RH in the Aula with near constant T and air pressure:

$$\theta_w = \frac{RH}{K_w + RH}, K_w = \frac{k_1}{k_2} \tag{2}$$

where K_w is the partition coefficient (equilibrium constant) of water molecules between the surface and the air, k_1 is the desorption rate constant, and k_2 is the adsorption rate constant of water molecules on/to the filter surface.

It was assumed that the surface coverage of water, θ_w, increased over the duration of the filter exposure in the Aula due to a decrease in k_1 and increase in k_2, and thus a decrease in K_w due to some particle deposition and resulting increasing deposits, and reactions, on the surface. This increase in θ_w could be described by more complex expressions of the changes of k_1 and k_2 with time. This seemed, however, of little use here as such expressions would introduce several additional constants and parameters that could not be determined from the relatively simple performed experiments. To illustrate the proposed hypothesis, it seemed sufficient to apply a simple exponential decrease of K_w with a time factor, k (h^{-1}), due to the deposition of the particles, gases, and (mostly) oxidising surface reactions, but with the inclusion of a term, K_{we}, for the endpoint (at $t = \infty$), to make it possible to determine a value for $\theta < 1$ at $t = \infty$. K_w then simply represents the water adsorption on the clean Teflon membrane filter at the start of the exposure. It is acknowledged, but not considered in this simplification, then, that the water adsorption may be of a more complex nature than filling up one monolayer, or might continue to several monolayers at high RH, as is typical on, for example, metals [37]. By combining Eq. 2 into Eq. 1, with an exponential decrease of K_w, Eq. 3 was then obtained:

$$K_s n = K_{oa} n \cdot \left(1 - \frac{RH}{(K_w - K_{we}) \cdot exp(-kt) + K_{we} + RH} \right) \tag{3}$$

In the model, the same value for the time factor, k, was used for all the five original SVOC model classes of the octanol partition coefficient $K_{oa}n$. This was done for simplicity's sake, and since further specifications were not possible based on the experiments, nor needed for the intended illustration of the hypothesis put forward. The manipulation of K_{we} allowed a slight raising of the model curve at endpoint at twelve months, and then a slightly better fit at three months.

The emission episode was simulated inside the original model as a similar multiple increase (m) at the time of the release in the instant concentrations of (i) all the five model classes of SVOCs ($[SVOC]_n$, n = 1 – 5), and (ii) of only the model class $[SVOC]_3$. This was followed by an exponential decrease in the concentrations at the rate of the air exchange (λ) in the Aula, of 0.9 h^{-1} [5], reported by the UiO real estate department (responsible for the maintenance of the Aula), according to:

$$[SVOC]_{n,e} = [SVOC]_n + (m \cdot [SVOC]_n exp(-\lambda t)) \tag{4}$$

Where $[SVOC]_{n,e}$ is the concentration in air of $[SVOC]_n$ with an emission episode. The estimated accumulating $PM_{2.5}$ mass deposit (D_p) was added to the mass of the SVOCs on the Teflon membrane filters, as $D_p = C_p$ x V_d, x t where C_p (g m^{-3}) is the particle concentration in the air and V_d (m s^{-1}) is the deposition velocity to the surface and t (s^{-1}) is the exposure time.

Results

Mass deposits on filters

Figure 2 shows the mass changes of the filters after exposure, the mass of organic carbon (OC) on the quartz filters found in the EC/OC analysis, and the typical water adsorption on blank Teflon membrane and quartz filters reported in the literature [38].

A decrease in the mass deposit with time on the Teflon membrane filters is observed in Fig. 2. The significance (by t-test) of the mass difference of the filters between three and six months was 86% in the original weighing, and 95% in the reweighing. After six months, the original measurements showed a possible continued negative trend in mass. The reweighed measurements, which might have been affected by some additional experimental uncertainty (see "Experimental uncertainty with weighing filters" section), did not exhibit this trend. The total deposited mass on the quartz filter was in the range of the deposited mass measured on the Teflon membrane filters. This indicated that a somewhat similar deposition had taken place on these closely positioned Teflon membrane and quartz filters.
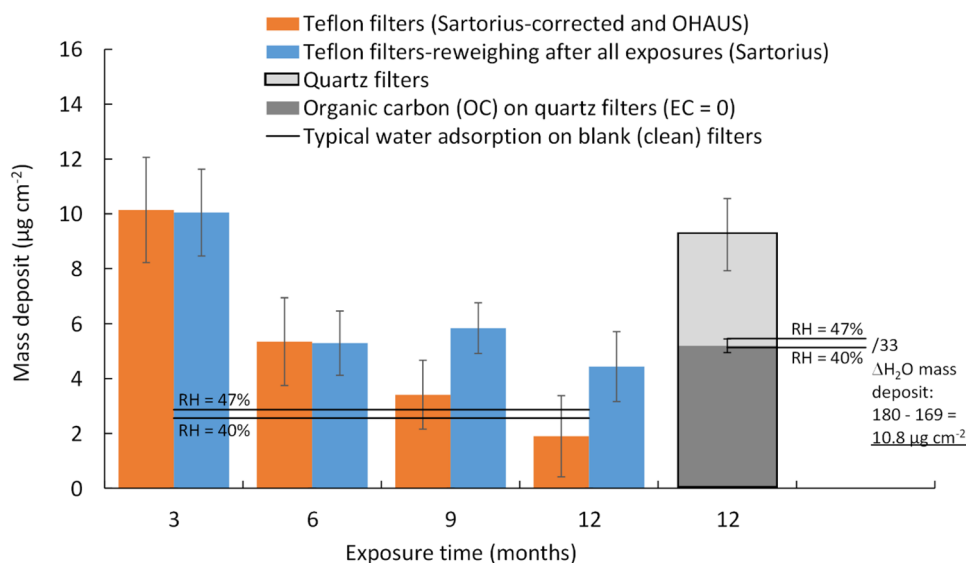
Fig. 2 The time-dependent mass deposits on the Teflon membrane filters mounted in the Aula, as of April 2021 (26.03.2021, Table 1), the annual total mass deposit, and organic carbon (OC) deposit on the quartz filters, and the expected weight increase due to water adsorption on blank filters at the RH at the initial (RH = 40%), and final mass measurement after twelve months (RH = 47%), at T = 18–22 °C, calculated from the literature [38]

Just over half of the measured mass change after twelve months on the quartz filters was found to be OC (5.2 ± 0.25 of the 9.2 ± 1.3 μg cm^{-2}, = 56%). No elemental carbon (EC) was detected (0 ± 0.07 μg cm^{-2}). The expected contribution from the recorded increase in RH to the deposited mass on the blank filters [38], between the initial to final weighing after twelve months (Fig. 2), indicated that the change in RH might be notably contributing to the additional 4.0 μg cm^{-2} deposited mass to that of the OC on the quartz filters. However, changes in the mass of adsorbed moisture due to the small changes in RH (Table 1) were probably not a major reason for the observed mass addition and its decrease after three months on the hydrophobic Teflon membrane filters, contrary to the hydrophilic quartz filters (Fig. 2).

Air pollutant measurements

Figure 3 shows the results from the air pollutant measurements. The typically opposing variations in NO$_2$ and O$_3$ annual concentrations for urban settings is observed in Fig. 3A. A higher [O$_3$] was observed in the spring and summer, when it is formed from the photolysis of NO$_2$. A higher [NO$_2$] was observed in the autumn and winter, when there is more emission from traffic combustion and residential heating, and less transformation to O$_3$. Figure 3B shows the respective indoor to outdoor (I/O) ratios of the gases. These were calculated from the periodic time averaged indoor concentrations from the passive sampling, with the annual value being the time-weighted annual mean of the periodic values, and the

averages of the diurnally resolved outdoor concentrations over the same periods. The figure shows the typical annual trends of the I/O ratios. The I/O ratios of NO$_2$ were observed to be higher than 1 in the summer, when NO and O$_3$ revert back to NO$_2$ in the relative indoor darkness. They were lowest in the winter, when outdoor emissions are high and photolysis low. Conversely, I/O values for O$_3$ are observed to be often lower in spring and summer, when it is formed outdoors from NO$_2$ and consumed indoor with NO, than in autumn and winter [23, 39]. The annual average I/O values of the gases were found to be I/O NO$_{2, av}$ = 0.68 and I/O O$_{3, av}$ = 0.67.

Discussion

Experimental uncertainty with weighing filters

Before interpreting the results, it is necessary to discuss the experimental uncertainty in the weighing of the Teflon filters. The uncertainty in the recorded deposited mass on the Teflon filters between exposure periods might be related (i) to the different balances used, (ii) to different humidity equilibration and moisture adsorption processes during weighing, and (iii) to possible material loss/deposition (contamination) before or during reweighing.

The difference between the Sartorius and certified NILU Mettler Toledo (and OHAUS) balances in the weighing of standards represented 2.1 μg cm^{-2} (or 23%) of the final reported result of the quartz filter. This difference indicated a possible systematic error in the recorded deposit on the Teflon membrane filters, which
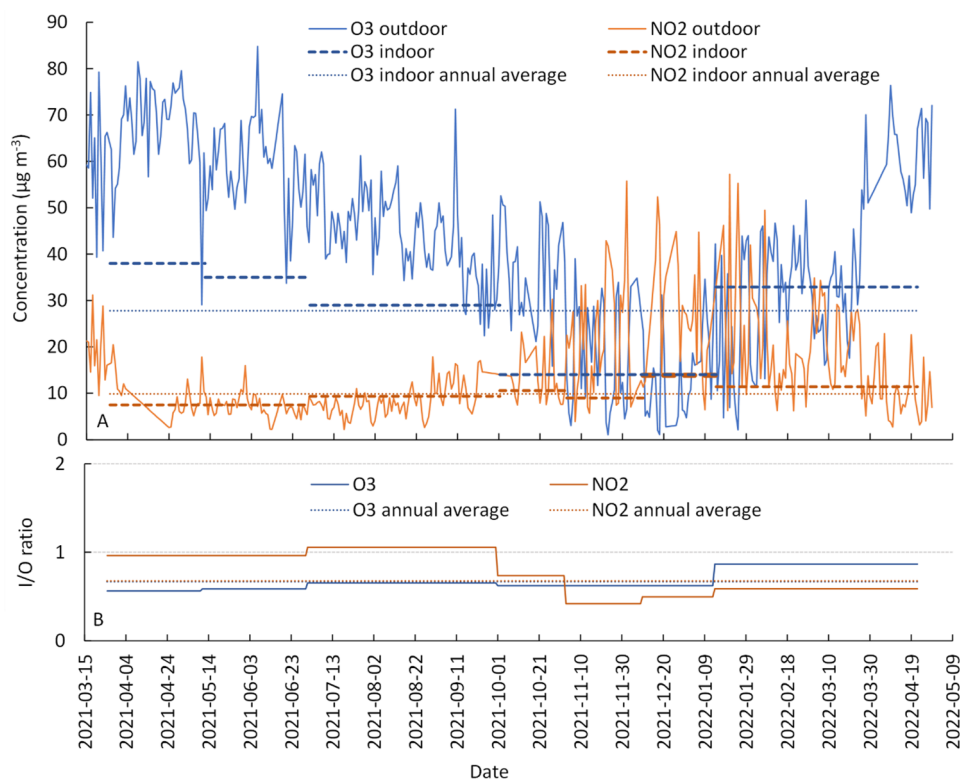
Fig. 3 Periodic mean concentrations **A** and indoor to outdoor (I/O) ratios **B** of nitrogen dioxide (NO_2) and ozone (O_3), outdoors from a nearby air quality monitoring station, and indoors measured with passive samplers over one year in the Aula

was calculated as the final masses from the OHAUS balance minus the initial masses from the Sartorius balance (Fig. 2). The mass correction by the standards of the initial mass on the Sartorius balance for the samples after three and six months' exposure seemed to confirm a higher accuracy of the final mass measured by the OHAUS balance, comparable to that of the NILU Mettler Toledo balance. This was, however, not the case for the samples after nine and twelve months' exposure, where the decreasing values as a result of the correction were much lower than the reweighed values. The reweighed values showed seemingly random variation between six and twelve months as compared to the original recorded values. The seemingly larger uncertainty in the measurements of the lower deposited mass readings from nine to twelve months could possibly be related to experimental errors of material loss or contamination in the reweighing, or to uncertainty in the correction between the balances. The evidence did not, however, seem to allow a definite conclusion on this.

A standard weighing procedure with 48 h humidity equilibration could not be followed due to accessibility restrictions (except for the quartz filters weighed after twelve months, see "Weighing and observation of filters" section). The equilibration of the quartz and Teflon membrane filters to the different humidity conditions during the weighing may thus have influenced their recorded mass (Fig. 2). It seems that any influence of the RH during weighing on the recorded mass changes of the filters between three and twelve months would depend on the association of a deposited organic film with moisture (as is further discussed in "The deposits on the filters" section).

We cannot exclude some effect of moisture adsorption due to (varying) laboratory RH levels during weighing. Despite these uncertainties, there seemed nonetheless to be a negative trend in the deposited mass measurements after three months.

The air pollutant sampling
The near-similar annual average I/O values found for NO_2 (I/O = 0.68) and O_3 (I/O = 0.67) were somewhat surprising given the higher reactivity, and typical indoor surface loss, of O_3 than NO_2. A previous modelling assessment reported NO_2 and O_3 I/O ratios of 0.6 and 0.5, respectively, from monthly measurements of NO_2 and quarterly measurements of O_3 in the winter of 2019. Based also on reported values from the nearby National Gallery, and in the literature, the annual average I/O values were suggested to be NO_2 I/O = 0.9 and
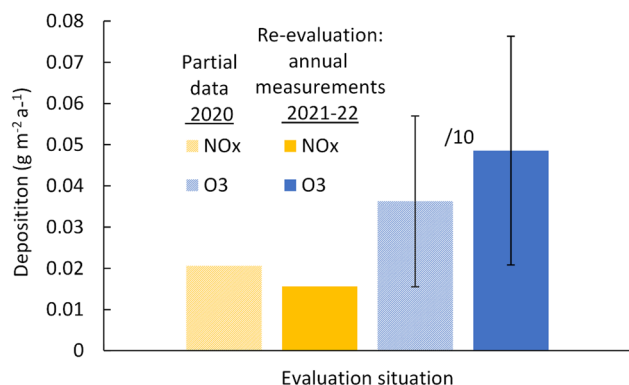
Fig. 4 Re-evaluation of the deposition rate of gaseous air pollutants from outdoors based on annual measured indoor values of the air pollutants. The O_3 deposition rate was calculated as the average within an assessed range of most likely indoor deposition velocities of O_3, with the uncertainty given by this range [5]

O_3 I/O = 0.5 [5]. The comparison of the results from the winter of 2019 and the present measurements indicates that the I/O ratios of NO_2 and O_3 are less different than could be expected from typical values including different locations. It may be that the I/O ratios of NO_2 and O_3 in the Aula are, generally, more similar than is typical. This may possibly be due to the large room volume relative to the surface areas, and the still air that would both limit the transport, and equalise the deposition velocities, of the gaseous pollutants to the room surfaces. It should, however, also be considered that air pollution concentrations in cities can have large local variations, and it is uncertain how well the outdoor concentrations from nearby air quality stations that were used in the calculations represent the concentrations at the air inlets of the Aula.

The measured annual indoor concentrations of NO_2 and O_3 indicated a mass deposition of the gases to the surface of the paintings in the Aula (calculated as the air-concentration multiplied with the same value of the deposition velocity in the two years of 2020 and 2021–2022) that was 75% (NO_2) and 135% (O_3) of that reported for 2020 by Grøntoft and Frøysaker [5]. Alternatively, this can be interpreted as on average 31 ($\pm$13–49) times more O_3 mass deposition compared to NO_2 in 2021–2022, rather than on average 17 ($\pm$8–28) times as measured in 2020 (Fig. 4). These revised values indicate a potentially larger risk from reactions of O_3 on the painting surfaces than was reported and discussed before, and should increase the concern about possible negative impacts of O_3.

The deposits on the filters

The sources of organic carbon (OC) on the filters could be from gaseous semi-volatile organic compounds (SVOCs) that are commonly observed indoors [16, 40], and possibly secondary organic aerosols, particulate matter, and dust from indoors or outdoors [41]. The particles might include CC that would be included with the OC in the analysis. A model has been proposed for the initial development of organic surface films on impenetrable, clean surfaces, involving the deposition and partitioning of SVOCs, which establish a film that "substantially alters the nature of the surfaces and imposes a degree of commonality within a few months" [16]. It is acknowledged that such clean surfaces are probably comparable to Teflon filters, but less so to soiled, painted surfaces. The expected subsequent development of a soiling layer has also been described as involving (i) a slower rate of deposition of fine inorganics, including salts and water-soluble particles, (ii) the oxidation of surface compounds, (iii) an increased water sorption/content, and (iv) the influence of acid/base reactions in the complex films of different porous surfaces [24].

The recorded deposited mass on the filters, besides that of the OC and excluding the EC that was not detected, could probably be attributed to, and affected by (i) adsorbed water, (ii) non-combustible inorganic compounds deposited as fine particles including salts, and (iii) the deposits and reactions of inorganic gaseous pollutants. An expected mass addition due to moisture adsorption on the blank quartz filters, from the initial weighing at 40% RH in the UiO laboratory to the final weighing at an equilibrium RH of 47% in the NILU laboratory (Table 1), would be 10.8 μg cm^{-2} (Fig. 2). That value is 270% of the 4.0 μg cm^{-2} additional deposited mass to the OC, measured on the exposed quartz filters (Fig. 2). The possible moisture adsorption on the quartz filters was thus much less than would be expected on blank filters. This may be due to the deposit of expected hydrophobic OC on the filters. Little adsorption of moisture is expected on clean (blank) Teflon membrane filters in an environment like the Aula's (Fig. 2). How the moisture adsorption developed in unison with a likely forming SVOC film on the filters seems uncertain and will be touched upon in the next section. Figure 5 shows an optical microscopy image of a Teflon membrane filter.

The optical microscopy of the Teflon membrane filters showed particles deposited upon them after all periods of exposure. Different types of particles were scattered over the surfaces. A rough distinction seemed to be between small, dark, near-spherical particles with a diameter of a few microns; brighter—and often also near-spherical,
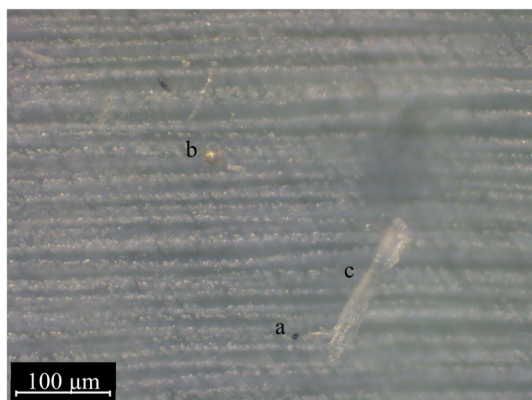
Fig. 5 Optical microscopy image, in raking light and ×200 magnification, of a Teflon membrane filter after twelve months exposure. The most typical particle types observed included: **a** small, dark, near-spherical particles, **b** larger, brighter, near-spherical particles, and **c** large, fibrous particles

but more irregular—particles with a diameter of c. 10–50 microns; and larger, wide/long fibrous particles, often several 100 microns in length. A quantitative measure of the particle surface coverage was not made. However, after three months only the smaller particles (<10 μm) were observed with the optical microscopy. After six months in addition, one large fibrous particle, similar to that in Fig. 5, was found. After nine and twelve months some more of the larger particles (>10 μm) were present. Despite lacking definitive evidence, the deposit of the different, particles seemed to increase with time, but not obviously so between nine and twelve months.

The surface adsorption of inorganic gaseous air pollutants, like O_3, was probably a small and un-notable influence on the deposited mass on the filters. However, an influence of the deposited particles, of inorganic gases (the deposition rate of which was expected to be several magnitudes higher than of $PM_{2.5}$ [5]), and of water adsorption on the recorded deposited mass on the filters *in combination* with the adsorption of SVOCs could not be excluded.

The decreasing deposited mass on the Teflon membrane filters over the period of exposure was surprising but was observed again in the later reweighing control of all the filters, which excluded the possibility that this change in mass was simply due to humidity variations at the times of weighing (Table 1). It was not possible to definitively explain this observation from the few analyses on the exposed filters, but rationalised explanations related to the likelihood of interactions between adsorbed and depositing compounds are discussed below.

A hypothesis on the initial film formation of soiling on unvarnished oil paintings

The deposition of air pollution to indoor surfaces happens as a simple function of a species' concentration in air, a deposition velocity (*see* "Mathematical model" section) that depends on the transport of the species in the air to the surface, and the properties of the surface [42]. In a simple model, without absorption into the surface or surface reactions, the gases will establish an adsorbed layer in equilibrium with the air concentration. Semi-volatile organic compounds (SVOCs) are expected to equilibrate and accumulate on an initially clean, impermeable surface at rates depending on their molecular mass, and establish a hydrophobic film of growing thickness and changing composition [15, 16]. This has been easily observed on, for example, glass surfaces [43, 44], that could be compared to the Teflon membrane filters, but less so to unvarnished, painted surfaces. Particles will not establish a similar air-surface equilibrium as gases, and the soiling, including adsorbed organic compounds, will generally accumulate over time.

It is here hypothesised, in accordance with Weschler and Nazaroff [16], that such a film of SVOCs—mainly from gases, but in a minor amount also from aerosols—adsorbed and was recorded as the deposited mass on the Teflon membrane filters at three months. An organic film with considerable molecular exchange (adsorption and desorption) with the air had then been established. In this case, the molecular exchange (sorption) and (theoretical) equilibrium of the adsorbed, and generally hydrophobic SVOCs on the surface, at any time would be expected to depend on: (i) the concentration of the SVOCs in the air, (ii) their association to the Teflon filter surfaces including the effect of the already present adsorbed SVOCs, (iii) the effect of any accumulating deposited particles that would include some water, (iv) the deposition and reaction with gases from the air, and generally (v) the reaction products that might accumulate on the surface over time, and (vi) the amount of adsorbed water (moisture) as affected by all these processes.

It seems likely that, over a year, such changes on the surface would systematically affect the number and affinity of surface sites available for SVOC adsorption, and thus affect the partition to, equilibrium, and amount of adsorbed SVOCs on the surface. The SVOCs' partition to the surface would probably increase in dry air (low RH) and decrease in humid air (high RH). It seems also likely that deposited particles would, generally, be more hydrophilic than the SVOCs, and contribute to decreasing the partition of the SVOCs to the surface from the air.
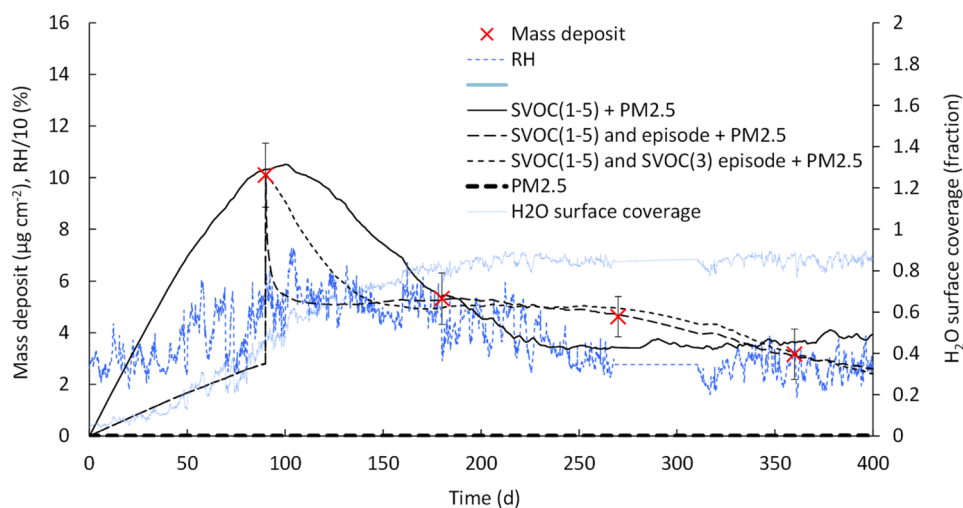
Fig. 6 Measured and modelled SVOC and $PM_{2.5}$ accumulated deposits, and water adsorption to Teflon membrane filters, and typical RH variation in the Aula, as of April 2021 (26.03.2021, Table 1)

In addition, surface oxidation of deposited SVOCs by the high concentration of O_3 in the Aula, or other oxidation agents, would probably take place, and could contribute to a less hydrophobic surface film over time. O_3 is known to especially oxidise unsaturated organic compounds, and as a result, it could be expected that low molecular weight, oxygen-rich carboxylic acids, like acetic and formic acid, would be among the surface reaction products [24, 45]. NO_2 has both oxidising and acidic properties, and in forming especially HNO_2 and HNO_3 on surfaces, it is expected to reduce the surface pH [24, 45].

On this basis, it is here hypothesised that the observed maximum mass deposit on the Teflon membrane filters after three months, and then the reduced deposited mass until twelve months, was due to a changing sorption equilibrium, and consequently reduced partition, to the filter surfaces from the air of SVOCs, which were present at concentrations that may possibly have been affected by emission episodes. The reasons for the reduced partition to the filter surfaces was then: (i) partly the variable effect of the changing RH in the Aula from the drier spring to the more humid summer, and (ii) partly an increasing hydrophilicity of the filter surfaces, and the presence of moisture. This increasing affinity towards water may have been caused by a combination of the accumulation of particles, and the oxidation of SVOCs on the surface by O_3 and other oxidants in the air, which made the surface more hydrophilic and "SVOC-phobic", so to speak.

Hypothesis testing by model fitting

This hypothesis was tested by the adjusted mathematical model that was described in "Mathematical model" section. Given the uncertainty in the recorded weights, it was decided to perform the modelling to an average of the "Sartorius mass-corrected" values and reweighed values (Fig. 2). Near-best, possible, manual fits of the models to the experiments are given in Fig. 6 to illustrate the hypothesis. It illustrates the model without emission episodes (Eq. 3 only), and the model with an emission episode of all SVOCs, as well as of just the class 3 SVOC, which had the largest influence on the SVOC partition to the surface (Eq. 3).

It is seen that both the models could reasonably fit the experimental results, but that the addition of an emission episode at the time of the highest measured mass deposit after three months could potentially improve the model fit.

Table 2 gives the default input values of parameters in the model from Weschler and Nazaroff [16], the changes in these input model values in this work (see "Rationale and implications of the adjusted modelling" section below), and the values of the three constants introduced in Eq. 3, needed to obtain the model fit without an emission episode (solid line in Fig. 6). The full, original model formulation, parameters, and typical values were described in detail by Weschler and Nazaroff [16], and their accompanying Additional file 2.

Different adjustments of the default and new model values could provide a roughly similar fit. Near-similar good fits could, for example, be obtained by changing the values of K_w and k inversely. The adjusted model values in Table 2 are thus not uniquely determined best-fitting values, but merely represent the model fit in Fig. 6.

The modelling of the $PM_{2.5}$ deposits in Fig. 6 seemed to correspond with the observations of the smallest photographed black particles (type (a) in Fig. 5). The mounted

Table 2 The model parameter default values from Weschler and Nazaroff [16] and their changed values, and the values of the new parameters in Eq. 3 as used in the scenario without an emission episode in this work

Model parameter	Default values	Adjusted values
Initial thickness of surface film (nm)	2	c. 0
TSP (total suspended airborne particle concentration) (µg m^{-3})	20	5
Volume fraction of organic matter in PM	0.4	0.1
Total air concentration (in gas + particles) of sorbing SVOC group 3 (µg m^{-3})	10	40
Time resolution (h^{-1})	1	0.5*
K_w (% with no direct physical meaning) (Eq. 3)	–	550
K_{we} (% with direct physical meaning) (Eq. 3)	–	4.5
k (h^{-1}) (Eq. 3)	–	0.025

*A double time resolution of the default was used to fit with the 30 min resolution of the RH data and improve the model curves

Teflon membrane filters had some slight curvature that might have facilitated deposition of larger, more gravitating particles. In this respect, they resembled the paintings. The paintings have been recorded to collect both fine particles and fibrous dust on topographic, textured features. The soiling happens both on features of the canvas showing through the lean, exposed grounds, and on features of the paints' pastose applications, and brush imprints (see Fig. 9) [46]. Less gravitational particle deposition, or none at all, would be expected on the quartz filters that were plane-fixed in designed instrument holders. As for the SVOCs ("Possible sources of SVOC emissions in the Aula" section, it could not be excluded that the filter mounting location had an effect on the particle deposition which could have been different than at the eleven paintings' surfaces throughout the Aula. The deposit of larger particles (> c. 10 µm) was only observed from six months onwards. Thus, an accumulation after three months and a possible resuspension thereafter of such particles seemed insufficient to explain the change in the recorded mass deposits from three to six months.

Figure 7 shows a breakdown of the five SVOC classes of the modelled mass deposits (that were summarised in Fig. 6). The model fittings depended mostly on the presence of the class 3 SVOCs, but also on all the classes (1–5) during the short time of their hypothetical high emission episode. With the passing of time the dependence on the presence of classes 4 and 5 increased relative to the other classes.

Rationale and implications of the adjusted modelling

The initial SVOC film thickness on the newly mounted Teflon membrane filters was set to c. 0 nm. The deposited film was measured as a mass change that would have not included an initial film. The main parameter adjustments from the model by Weschler and Nazaroff [16] featured a lower indoor total particle concentration, and a lower SVOC partitioning from the air to these

particles. As soiling of the paintings in the Aula by particle deposition is a major issue, the air in the Aula is filtered with an efficiency of about 80% [5]. An effort has also been made to reduce the particles brought in by visitors. The particle concentration in the air has not been measured, but it is hypothesised here that it was much lower than the default total suspended airborne particle concentration (TSP) value of 20 µg m^{-3}, and it was set to
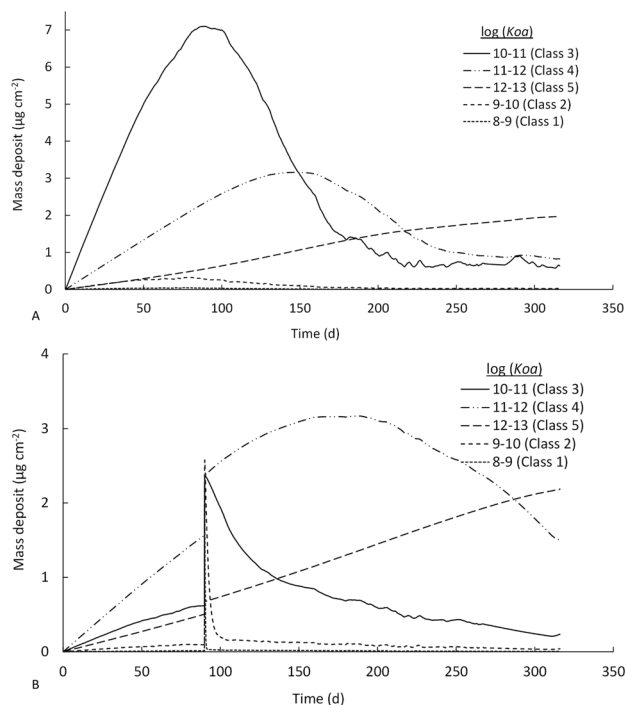

Fig. 7 The adjusted modelled SVOC mass deposit as of April 2021 (26.03.2021, Table 2) of the five SVOC classes to the Teflon membrane filters, defined by their average octanol–air partition coefficients, with adjustment of the octanol air partition coefficients depending on (**A**): surface humidity (Fig. 6, SVOC(1–5) + Eq. 3), and (**B**): addition of the [SVOC]$_{1-5}$ emission episode after 3 months exposure of the filters (Fig. 6, SVOC(1–5) and episode, Eqs. 3 and 4)

$TSP = 5 \, \mu g \, m^{-3}$. It was then assumed that $TSP/PM_{2.5} = 3$. This is double the value of the $PM_{10}/PM_{2.5}$ fraction, of 1.5, which was measured in the nearby National Gallery (Oslo) in 2010 [47]. A $TSP/PM_{2.5}$ fraction of 3 seemed reasonable from the qualitative observation of larger deposited particles (than PM_{10}) on the Teflon filters (and paintings), but measurements would be needed to determine this. It would represent a $PM_{2.5} = 1.7 \, \mu g \, m^{-3}$, which was found to be the lower probable concentration of $PM_{2.5}$ in the Aula in 20,205. The deposition of fine particles ($PM_{2.5}$) on the vertically oriented filter surfaces was expected to be low. Considering a typical $PM_{2.5}$ deposition velocity to a vertical room surface without thermophoresis of $5 \times 10^{-5} \, cm \, s^{-1}$ [16, 48], and average concentration, the annual deposition to the filters would be $0.003 \, \mu g \, cm^{-2}$, which was very little compared to the recorded mass changes (Figs. 2 and 6). The variation in the outdoor $PM_{2.5}$ concentration during the exposure period was from a minimum of $4 \, \mu g \, m^{-3}$ on 1st April 2021 to a maximum of $16 \, \mu g \, m^{-3}$ on the 1st December 2021 at the closest air quality monitoring station in Sofienbergparken [28], and would not change this assessment. The deposition of larger particles to the vertical surfaces was expected to have been even less [49]. It seemed however from the observation of the Teflon membrane filters that some slight curvature and/or possibly the surface structure of the filters (see "Hypothesis testing by model fitting" section) may have resulted in more deposition of larger particles than this theoretical assessment. The observed monotonic accumulation of these larger particles could, however, not explain the reduced mass addition on the filters after three months exposure. A theoretical assessment of its amount seems uncertain and unnecessary in the hypothesis testing, and was therefore not pursued here.

There was no data for the partitioning of SVOCs to these particles, but the notable amount of (hydrophilic) salts that has been measured on HVAC filters, may indicate a lower value (than the default of 0.4). Lastly, the concentration of the class 3 SVOCs had to be considerably increased for the adjusted model without an emission episode (Eq. 3) to fit the seemingly high mass deposits measured on the Teflon membrane filters after three months. SVOC concentrations in the Aula have not been measured.

The model fits including an emission episode (Eqs. 3 and 4) were obtained by using the default model values, in addition to a value of *m* to increase the concentrations during the episode, and slight changes of the three adjusted model input parameter values, K_w, K_{we} and k, from Table 2. To obtain a mass deposited during emission episodes equal to that measured after three months on the Teflon membrane filters, emission strengths (*m* in Eq. (4)) of $\times 428$ the $[SVOC]_{1-5}$ (Fig. 6, SVOC(1–5) and episode, Eqs. 3 and 4), and $\times 1\,780$ the $[SVOC]_3$ (Fig. 6, SVOC(3) episode, Eqs. 3 and 4) model default concentrations were needed at the time of the emission episodes. This gave total concentrations of the SVOCs over the 30 min period of the emission episode, equal to the time resolution in the modelling, of c. $20\,000 \, \mu g \, m^{-3}$ ($21\,600 \, \mu g \, m^{-3}$ in the case of the $[SVOC]_{1-5}$, and $17\,700 \, \mu g \, m^{-3}$ in the case of the $[SVOC]_3$). In the case of the $[SVOC]_{1-5}$ emission episode, the percentage distribution of the SVOC model concentrations, between the $SVOC_1$ to $SVOC_5$ groups during the episode was: 40%, 30%, 20%, 9%, and 2% (at 90 days in Fig. 7B). In the case of the emission episode of only $[SVOC]_3$, the model concentrations during the episode consisted of close to 100% $SVOC_3$.

High TVOC (total volatile organic compound) concentrations have been measured in other museums. In a location with high emissions, though not through a singular emission episode, a TVOC concentration of near 5 000 $\mu g \, m^{-3}$ (4 680 $\mu g \, m^{-3}$) was measured over 40 min in an art gallery in Germany [49]. A sudden SVOC concentration of c. $20\,000 \, \mu g \, m^{-3}$ during an emission episode (of 30 min) in the Aula seems like a very high concentration. The possibility of contributions from emission episodes to the observed mass deposit on the Teflon membrane filters is discussed below.

Possible sources of SVOC emissions in the Aula

Available records of cleaning and housekeeping products normally used in the Aula included floor waxes and surface oils, floor and carpet cleaning detergents, and sanitation detergents. The chemical product descriptions included both mixes of individual reagents, like acrylate polymers in floor waxes, and specific compounds identified only by their CAS numbers. It was possible to find values of the octanol–air partition coefficients (K_{oa}) of only a few of the identified reagents in databases [50, 51]. These databases showed that most compounds with an octanol–air partition coefficient in the range of log (K_{oa}) = 10–11 typically have a molecular weight of u = 400–600. This includes the class 3 SVOCs that had the largest influence on the SVOC film formation on the Teflon membrane filters (Fig. 7). Several ingredients with a notable percentage concentration in the cleaning products could be considered in this range, for example, prevalent compounds in the floor wax used in the Aula[3]: acrylate copolymers (2–5%), and linked(poly)-alkane waxes (1–2%) probably have a range of molecular weights due to their polymeric character; montan-wax-fatty-acid-ethylene-ester (u = 469) (1–2%), and tris(2-butoxyethyl)

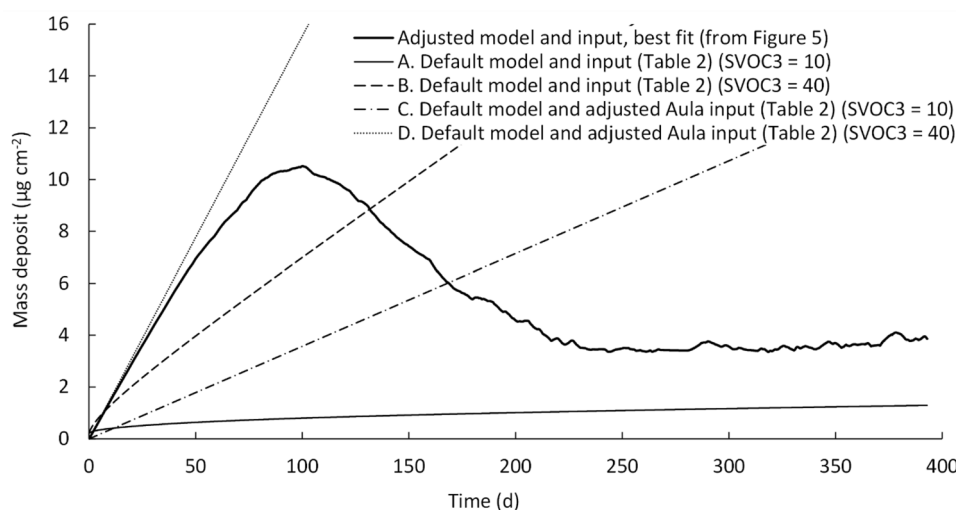[3] S-wax, data sheet found in Additional file 3.

Fig. 8 The best fit to experiments of the adjusted model in this work, without an emission episode, compared with the deposit predicted by the default model for some situations

phosphate (u = 398.5) (0.2–0.5%). It seems such products have a composition to potentially volatilise and substantially adsorb to different surfaces than where initially applied. Chemical analysis of such deposits should give more information about their composition and the sources but was not attainable in this work.

Notable SVOC emission episodes from cleaning and maintenance may have occurred during the filter exposures. The Additional file 2 details all the documented events and associated cleaning episodes that took place in the Aula during the duration of the exposure experiment. Discussions with the Aula senior curator and the housekeeping team indicated that cleaning episodes took place before and after any public event. Cleaning methods followed regular daily housekeeping practices: dry cleaning with microfibre-mopping for dust capture; vacuum cleaning with HEPA-filters; use of a damp mop impregnated with wax, but no use of chemical cleaning agents like strong household detergents or bleaches. Notably during this period, there was no dedicated waxing campaign of the floors due to the pandemic. It is possible that these housekeeping practices may have released SVOCs near the filters. As the filter exposure took place mainly during the period of COVID19 restrictions, there may also, for example, have been some use of disinfectants on nearby surfaces such as the gallery balustrade.

Such different SVOC emissions may have occurred more or less continuously (Eq. 3), periodically, or restricted to episodes (Eq. 4). From available schedules and records of the cleaning activities in the Aula (Additional file 2), it was found that the first three months of exposure featured the least amount of cleaning episodes, as a result of fewer events taking place in the Aula. In the

second and third exposure periods, up to six and nine months, the Aula saw an increase in events, visitors, and probably resultant environmental changes. It featured increasing housekeeping and cleaning episodes from the second to the third period. These then diminished over the last quarter of exposure. It is possible that despite the lower regularity of cleaning in the first three months of exposure, a high concentration emission episode may have occurred. It seems likely that the measured mass deposits over the year were affected by the Aula's events schedule and SVOCs emissions from housekeeping and maintenance, but a specific emission episode that could explain the mass deposit maxima on the filters after three months' exposure was not identified.

It cannot be excluded that some unknown emission sources, and/or that the proximity of the filters to the gallery floor, which might have had air flow conditions different from those along the wide walls and paintings, may have contributed to higher concentrations and deposition of SVOCs.

Model limitations and implications for soiling on unvarnished artworks

The main constraint in the fitting of the adjusted model seemed to be the maximum film thickness, as well as the start time of the decrease in the film thickness, which was measured experimentally to happen between three and six months. Figure 8 compares the model fit in this work with the deposit predicted by the default model for some situations. The default model predicts a monotonically increasing deposit and SVOC film thickness.

The experimental mass deposits on the Teflon filters seemed relatively high when compared to the default
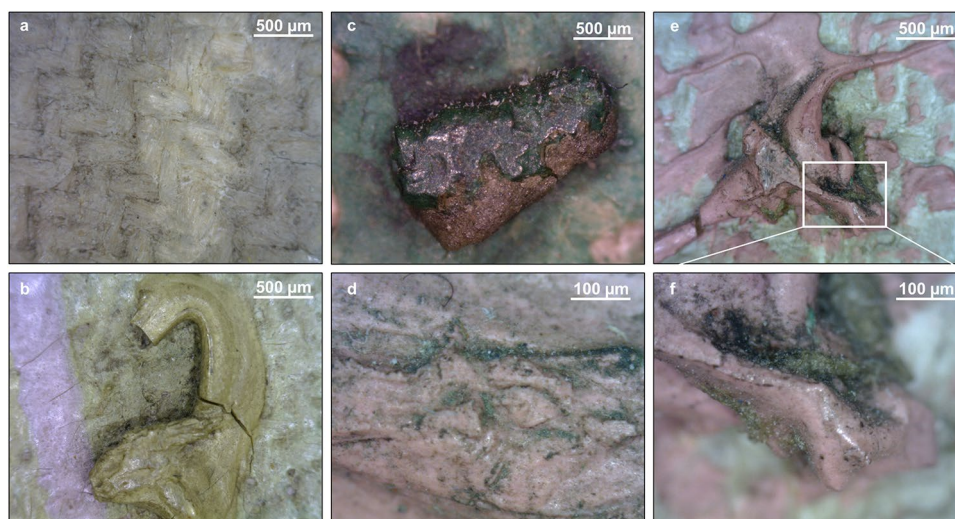
Fig. 9 Various examples (**a**–**f**) of microscopic particulate soiling observed on the surface of the Aula painting *Kjemi* (E. Munch, 1914–1916, 450×225 cm, Woll no. 1227, UiO). Example **a** shows an area of exposed ground, whereas examples **b**–**f** illustrate passages in oil paint. Example **f** shows a detail of the area highlighted in example (**e**)

model (Fig. 8A), and also when using the expected values of the environmental parameters in the Aula (Fig. 8C), but were especially not all out of range when somewhat higher SVOC concentrations (Fig. 8B and D) were considered. It seems probable that the total observed accumulating particle deposition, including particles larger than $PM_{2.5}$, contributed more to the final mass after twelve months than first assessed for $PM_{2.5}$ (in Fig. 6). If the non-SVOC deposits of particles larger than $PM_{2.5}$ had been included in the modelling, these would likely have affected to some extent the adjusted modelling parameter values in Table 2. The evidence—especially of the OC deposit on the quartz filters exposed in parallel—strongly suggests that a mechanism of SVOC deposition like that proposed in this work could explain the mass deposition on the Teflon filters. More experimental evidence is however needed to verify or falsify this.

At some time after three months, and possibly after the year of experimental measurements on the filters, one would expect the mass deposit to reach a minimum with a minimal SVOC film. The mass deposit would thereafter probably increase slowly due to slow particle deposition on the remaining film of less volatile and partly oxidised organic compounds. Reported large amounts of lighter molecular weight VOCs in an aged, organic film on glass in a museum indicated that the composition of such established films can be complex, and include much higher amounts of volatile compounds than expected from their singular partitioning coefficients [45].

As an organic surface accumulates soiling, and reacts with air pollutants, like the potentially damaging nitrogen oxides (NO_x) and ozone (O_3) [24], it would thus become less hydrophobic with more adsorbed moisture. This would in turn facilitate further deposition of particulates and gaseous air pollutants, and chemical reactions. A painting surface could in this manner become more hydrophilic and acidic, as a result of, for example, chain scission in ester linkages in the binder, as observed on aged canvases [45]. Further complex surface reactions between air pollutants, soiling, and painting materials could be expected [16, 42]. Over longer time periods, a soiling layer with fine particles bound with heavy organic compounds could result, such as that which has been observed on the Aula paintings [3, 5], together with a moisture film of a thickness depending on the RH. As the soiling layer increased, it would also undergo other physicochemical changes—for example becoming harder due to further oxidation, cross-linking and bonding, cementation, and reaction with surface substrates and so on—that would further deteriorate the artwork's surfaces. The result of these processes in the long term has been the variably tacky, acidic, and hydrophilic soiling layers that have been observed to be so difficult to clean from Munch's Aula paintings [18] (Fig. 9). Clearly, more investigations are needed to understand such surface film development.

Implications of hypothesis for the care of unvarnished oil paintings on canvas

The hypothesis proposed here has implications for the care and preservation of unvarnished artworks, including examples such as the monumental Aula

paintings. The possible role of SVOCs in the formation of fine soiling layers might form the basis for more extensive monitoring of these chemical species in exhibition spaces displaying unvarnished artworks featuring oil on canvas. Such monitoring might include a closer study of the effect of cleaning routines, which use organic and possibly volatile polishes, waxes, and other cleaning products, on the formation of SVOC films, as well as further studies on the relationship between air pollution and particulate deposition onto vertical surfaces. Given the postulated role of SVOCs in the formation of soiling layers it could, if not already practiced by an institution, be of benefit to incorporate the list of materials used in gallery cleaning within preventive conservation strategies and investigate the means of maintaining as low as possible SVOC concentrations.

The point raised by this discussion is the potentially complex role of relative humidity on the formation of SVOC and particulate matter films. The modelling carried out in this study has indicated that the moisture content in the air might be important in relation to the adsorption and partition coefficients of SVOCs to surfaces. If, by further evidence, the equilibria at play as described in Eqs. 1, 2 and 3 are found to influence the SVOC film formation and related effects on paintings, it might be possible to shift them beneficially by directly managing the RH within an indoor space. This would seem to depend on the possible detrimental role of the adsorbed SVOCs in combination with, and relative to, the surface moisture. Oxidation of SVOCs might increase surface hydrophilicity/acidity, and thus increase the likelihood and rate of particulate matter deposition. Increasing moisture adsorption with higher levels of RH could mitigate against the initial adsorption of SVOCs to a painted surface and its possible later negative effects, but the higher moisture adsorption might also increase soiling and degradation rates. It seems thus essential to understand the non-trivial combined and relative effects of the SVOCs and RH levels.

At lower RH levels, and given a certain concentration of SVOCs, it is likely that SVOC adsorption to surfaces is promoted initially. Under such conditions, it could be beneficial to target the role of gaseous pollutants, such as O_3 and NO_x, in promoting increased surface hydrophilicity, deposition of acidic and/or hydrophilic particulate matter, and soiling film formation. In this case, the concentration of ozone could be actively managed for example through the use of museum-appropriate ozone scavengers like active carbon filters [12, 14, 52, 53].

Ultimately, the hypothesis presented in this paper indicates that the maintenance of low levels of SVOCs and ozone and related oxidising gaseous pollutants in indoor spaces, together with an appropriately low RH (in balancing the other preventive needs of unvarnished oil paintings on canvas), could reduce the rate of development of increasing surface hydrophilicity and moisture adsorption, which in turn would mitigate against soiling films on unvarnished painted surfaces from becoming more obstinately fixed. A further understanding of the complexity of the mechanisms of film formation and soiling deposition would serve to elucidate the processes at play.

Conclusion

A first-year mass deposit from the air of 3 µg m^{-2} was measured on Teflon membrane filters exposed vertically by Edvard Munch's unvarnished oil paintings on canvas in the University of Oslo Aula, decreasing from 10 µg m^{-2} measured after three months. A first-year mass deposit of 9 µg m^{-2} was measured on quartz filters—with 5 µg m^{-2} found to be organic carbon (OC) and no elemental carbon (EC) detected, and the remaining 4 µg m^{-2} probably attributable mainly to adsorbed water. By fitting the measured data to a published model, it was hypothesised that the observed mass deposits were due to the establishment of a film of semi-volatile organic compounds (SVOCs) deposited from gases mainly, and in small quantities from particles. By adjusting this model's parameters whilst fitting the data, it was further hypothesised that the decrease in the mass deposit with time was due to a decreasing partition coefficient of the SVOCs to the filters from the air due to increasing water adsorption on the filters, possibly in combination with an (or several) early emission episode(s), and higher SVOC air concentrations during the episodes. The hypothesised increasing water adsorption might have been due to two main factors: (i) the filter surfaces may have become less hydrophobic as some fine particles adsorbed to the surface, and as the depositing organic film reacted with the comparatively high presence of ozone in the Aula compared to many indoor locations, and (ii) the relative humidity (RH) in the Aula which increased from the start of the exposures in late winter/early spring to the summer. The observations did not support an alternative hypothesis of reduced mass deposits on the filters after three months due to resuspension of particles/dust, and it was found unlikely to be due to contamination from the handling of the filters. Future research should search to describe the deposited particles including the contribution of particulate carbonate in more detail. SVOC film formation is possibly an important part of the initial

soiling film formation, for example, after surface cleaning that may reoccur on the Aula paintings. These observations have implications on the preventive management of indoor environments for unvarnished oil paintings on canvas and indicate the possibility of more complex soiling deposition mechanisms than previously considered.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-023-01115-y.

Additional file 1. Measured mass deposition tables.

Additional file 2. Cleaning activities by exposure period.

Additional file 3. S-wax MSDS (in Norwegian).

Additional file 4. Estimated RH from outdoor AH.

Availability of data and materials
The experimental data are available in Additional file 1. RH data from the Aula might be obtained from Conservation Studies, IAKH—University of Oslo on kind request from the authors.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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

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