



Ammonia chemistry within Danish churches

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ABSTRACT

The increase of agricultural intensity over the last century in rural Denmark has meant that ammonia has been regarded as a significant environmental problem. The deterioration of murals in rural churches is also a matter of concern and focused attention on the potential for ammonia to accelerate damage. Ammonia concentrations measured over 12 months inside and outside nine churches often show a spring maximum outdoors, hinting at the importance of farming activities. The ammonia concentrations are on average some three times greater indoors than outdoors and mass balance calculations suggest that this arises from the decomposition of ammonium nitrate aerosols. The emissions may result from reactions of aerosols deposited at the alkaline walls, which also leads to calcium nitrate becoming the major soluble salt at the very surface layer. The quantities remain small enough, that they probably do not participate in salt damage to the murals.

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1. Introduction and research aim

Most Danish churches from medieval times have had some kind of mural decoration. After the protestant reformation swept Denmark in 1536 some of the murals were whitewashed, although the iconoclastic movement was not nearly as prolific here as for example in England and Switzerland (Lilie, 1992). The habit of decorating Danish churches with murals was also maintained after the reformation. However, the majority of the murals became whitewashed in the period from 1650 to 1800, an activity that intensified toward the end of the 18th century. By the start of the 19th century almost all churches were whitewashed inside. This state of affairs lasted only shortly. Starting in 1823 the hidden murals began to be uncovered (Lind et al., 1930–1960) by removing the old lime wash with a spatula and sometimes a hammer to chip off the covering. No chemical agents were and are normally used in cleaning, but sometimes the murals were stabilized with: 1/ casein (brushing with skim milk), 2/ thin lime wash (inspired from England), 3/ water glass (very rarely) and 4/ also very rarely *Carlsberg-præparat* (Brajer and Glastrup, 2008).

After restoration, deterioration set in both the newly restored murals and the few that had escaped whitewashing. The rate of damage appears to have increased since the 1940s when photographs and closer observations began to be made. A small amount of damage arises through soiling and biological attack deriving nutrient from

deposits. However, the main route to deterioration appears as salt damage, which is exacerbated by church heating that began in the 19th century. Dampness within the walls and vaults typically is derived from roofs leaking onto the top of the vaults and penetrating behind the murals. In unheated churches of the Middle Ages there was little difference between inside and outside temperatures of the vaults, but with church heating evaporation from the inside walls led to the deposition of salts. The salts may have been present in medieval bricks, be drawn from the ground water, or derived from sea-salt particles deposited onto the exterior surface of the vaults. The repeated crystallization and deliquescence of the salt weathers the murals (personal communication, Kirsten Trampedach, National Museum of Denmark).

Over recent years there have been fears that murals in Denmark have been damaged and the increased emission of ammonia has been seen as a potential culprit. The ammonium concentration in the atmosphere has increased by a factor of 2.5 in 110 years (1870–1980), probably due to increased livestock and use of inorganic fertilizers (Hovmand, 1990). In Scandinavia Birkeland pioneered the fixation of nitrogen using the arc-process (Earnst and Sherman, 1927) to produce calcium nitrate or *Norgesaltpeter*, but the major fertilizer used was *Chile-saltpeter* (NaNO₃) which constituted 70% of the world consumption of N-fertilizer 1850–1910. The increased use of inorganic fertilizers might transfer nitrate to rural churches while the expansion of livestock in Denmark has increased the flux of ammonia to the air (e.g. Fowler et al., 2004).

Bak et al. (1999), in a report *Natur- og miljøeffekter af ammoniak* for a Danish ministry, suggests ammonia was one of the country's

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biggest environmental problems in the open countryside. Conservators and restorers see ammonia as a damaging agent because of its destructive effect on modern whitewashed walls. They are also discouraged from using ammonia solutions for cleaning, as ammonia may react with various organic compounds discoloring the mural and reducing the cohesion of the binding matrix (Dei et al., 1996). Airborne ammonia brought into the church building from the outside air is also recognized as mediating in microbial damage (Khadzhivulcheva and Markova, 1983; Eckhardt, 1985a,b; Petushkova and Lyalikova, 1986; Bock et al., 1988; Pique and Dei, 1992). However, the deterioration of the murals can also be caused by temperature changes, moisture, salts, atmospheric pollutants and growth of bacteria and fungi (Garg et al., 1995). Sulfur dioxide, ammonia, dust, oxidants and metal aerosols were long ago blamed for the deterioration of Russian murals (Doichinov and Khadzhivulcheva, 1981).

The aim of the present study was to clarify the potential for ammonia to have direct or indirect effects on the deterioration of the murals in Danish churches. Hence measurements of the indoor and outdoor concentrations of ammonia were undertaken simultaneously in nine churches throughout a year although here only in two of them extensive studies are reported in detail including measurements of wall chemistry and pH at these locations. The temperature and relative humidity (RH) were measured simultaneously in the indoor environment, and the practices of maintenance of the churches were recorded.

2. Selection of the churches

Ammonia was measured both indoors and outdoors at nine churches throughout a year (locations shown in Fig. 1 along with some relevant characteristics in Table 1). The churches range from a cathedral, Haderslev, to small rural churches spanning both different ammonia emission regimes and geographically over Denmark. One church, Sæby, underwent restoration during part of the measurement period during which ammonia was used by the workers inside the church which resulted in much increased concentrations.

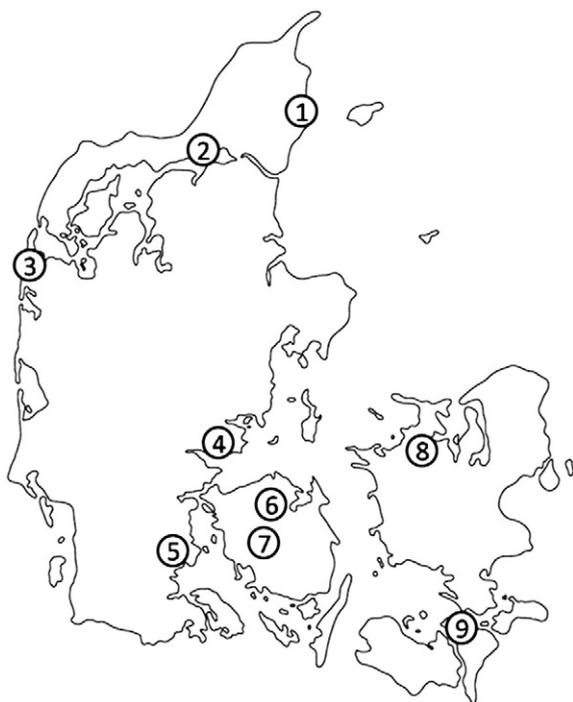


Fig. 1. Map showing locations of the chosen Danish churches. 1: Sæby Church, 2: Gjørl Church, 3: Dybe Church, 4: Vrigsted Church, 5: Haderslev Cathedral, 6: Sønderø Church, 7: Nr. Broby Church, 8: Gislinge Church, 9: Kippinge Church.

We have targeted two medieval churches for closer investigation, Nr. Broby Church and Sønderø Church, both on the island of Funen (Fig. 1). Nr. Broby Church is situated in the center of a small village, which is surrounded by farmland. However, there is no apparent nearby strong contributor to ammonia in the vicinity. The murals were last restored in 2003 and the locations on the walls that we study here were whitewashed at the same time. These lime walls cover almost half of the interior area of the church. Sønderø Church lies on the outskirts of a small town and near the surrounding farmland. It is a fairly large church with two side aisles with a reasonable amount of ecclesiastical activity. A farm is situated nearby as well as two main roads with some traffic. The recovery of the murals began in 1898 and they were restored again in 1933. Floor plans of the two key churches are given in Fig. 2a and b.

3. Analytical methods

The present investigation included measurement of ammonia concentration indoors and outdoors of the nine churches. Monitoring the temperature and the relative humidity (RH) was also undertaken inside all nine churches (although measurements not reported here), whereas measurement of air exchange rates and validation of ammonia measurements were done in both Nr. Broby and Sønderø churches.

3.1. Ammonia measurements

The majority of the ammonia measurements were carried out by passive sampling using ALPHA-diffusion samplers® (Adapted Low-cost Passive High Absorption, Tang et al., 2001). The working principle of the sampler is passive diffusion; where air is filtered through an outer Teflon filter (5 µm PTFE membrane, 27 mm diameter), followed by a 6 mm gap to an inner filter impregnated with 50 µL of citric acid (13% w/v in methanol). During exposure the ALPHA-samplers were attached by Velcro to a 4 mm thick disk made of hard plastic. All measurements were done in triplicate, meaning that three ALPHA-samplers were attached to each disk. The disks were housed under an upside-down stainless steel bowl mounted on a 1.5 m high steel pole for the outdoor measurements and placed in a way that the rims of the ALPHA-samplers were in line with the rim of the bowl. During indoor measurements the disks were typically at the same height as the murals, now with the open end of the ALPHA-samplers pointing upward. During the measurement period which lasted for 1 year (November 2007 through November 2008) the ALPHA-samplers were replaced once a month or occasionally more frequently.

Every part of the ALPHA-sampler except for the citric acid filter was reused. Between measurements the casings (all parts included) were washed in Deconex® laboratory detergent, and rinsed and dried before reassembly. The Teflon filters were cleaned in an ultrasound bath for 15 to 30 min with a little iso-propanol added to prevent the filters from sticking together due to static electricity. When assembled the ALPHA-samplers were stored in individual zip-lock bags both before and after exposure and transported in glass jars. After exposure the Teflon filter and the ring securing it to the casing were replaced with a plain plastic lid. This was done in order to avoid post-measuring uptake of ammonia originating from decomposition of the particles adhering to the outer filter. On arrival at the laboratory the citric acid filters were removed from the casings and transferred to plastic bottles and stored in a refrigerator until analysis. Just prior to analysis the filters were extracted in 3 mL of deionized water for 1 h on a mechanical shaker. The analysis for NH_4^+ was carried out on a Dionex ion chromatograph.

To verify the concentrations determined by the passive samplers and at the same time determine ammonium nitrate particle concentrations, a series of simultaneous measurements using both passive

Table 1

Characteristics of the churches. Approximate interior volume of churches' room, number of churchgoers per year, number of churchgoers per year per m³ of interior volume of the church, number of airings per year, state of preservation: 1 = state of murals is satisfactory, 2 = possibly in need of treatment/restoration/conservation, 3 = in need of treatment/restoration/conservation, 4 = acute need of treatment/restoration/conservation and annual ammonia concentration indoors and out.

Church	Interior		Churchgoers		Airings	Preservation	Annual NH ₃	
	Volume m ³	Area m ²	a ⁻¹	m ⁻³ a ⁻¹	a ⁻¹		Indoor	Outdoor
Dybe	710		1700	2.4	13	1	6	1.7
Vrigsted	880		1900	2.2	364	1	3.5	3
Haderslev	15,980		49,600	3.1	26	2	5.2	2.3
Søndersø	1680	1643 ^a	7100	4.2	104	2	5.6	1.7
Sæby	3660		14,800	4	52	3	9.1	1.5
Gislinge	760		5800	7.6	52	3	6	1.9
Gjøl	1240		11,000	8.9	364	4	4.4	4.8
Kippinge	1130		3200	2.8	250	4	3	1
Nr. Broby	1260	1553 ^a	12,200	9.7	13	1/2	5.6	1.6

^a This represents the total area inside the church, not just the walls.

and active samplers simultaneously were carried out. The active sampling was carried out using a batch denuder system (Ferm, 1979), where air was sucked through glass tubes covered by a receptive medium (here oxalic acid) and set in series of two or three tubes. Prior to analysis the tubes were extracted in 3 mL deionized water and treated as the ALPHA-sampler extracts.

In the validation procedure the denuder measurements were carried out in doublets and the ALPHA measurements in triplicates. The results (details not reported here) show that the values derived from the ALPHA-samplers are 40%±10% lower than the denuder measurements. A further investigation regarding the effects on the ALPHA-sampler measurements of the possibly different conditions between the churches is advisable, but as we are here mainly

interested in the variations between the ammonia concentrations of the various churches and not the exact absolute value a simple factor correction is sufficient. Accordingly we have applied a constant correction of +40% to the data obtained by ALPHA-samplers. The systematic difference between the indoor measurements performed with the denuder system and the ALPHA-samplers is probably caused by a restricted indoor air movement inside the churches as compared to outside the churches.

3.2. Air exchange rate measurements

The air exchange rate was needed for mass balance calculations. This was established by utilizing CO₂ concentration decay data. The

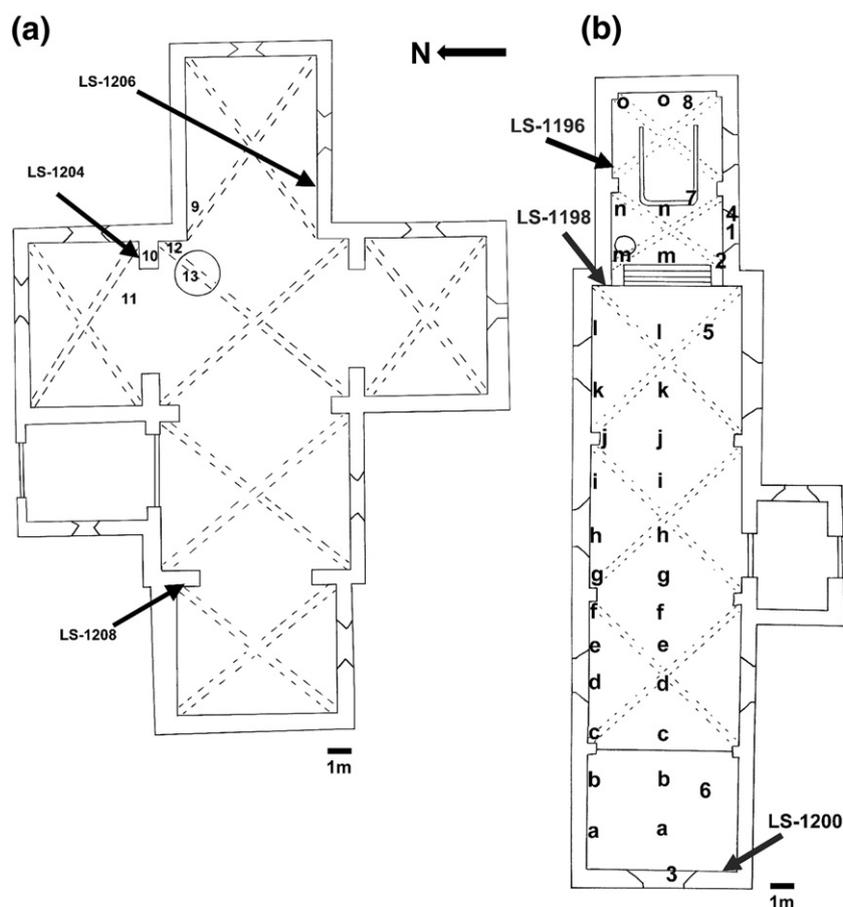


Fig. 2. Plans of (a) Søndersø and (b) Nr. Broby churches showing sampling points.

analysis was performed by the use of a Vaisala CO₂ sensor (range 0–5000 ppm) (Vaisala Oyj, Vantaa, Finland) connected to a Tinytag datalogger (Gemini Dataloggers, Chichester, United Kingdom). In Nr. Broby Church on one occasion CO₂ was released from a compressed gas cylinder to about 3000 ppm, and mixed into the room air using an electric fan; the concentration decay rate was subsequently monitored for the empty church over 48 h. On four more occasions the decay rate of metabolic CO₂ from churchgoers was monitored in the hours following a service, after the church had been emptied for people. From these measurements the air exchange rate was calculated on the basis of peak CO₂ concentrations of 900–1600 ppm. The ambient CO₂ level (background) was measured with the same type of sensor from an open shed near the church. At Søndersø Church the air exchange rate was similarly measured by monitoring the metabolic CO₂, and here the air exchange rate was also measured during an incidence of airing the church.

3.3. pH-measurements of indoor surfaces

The pH was measured on selected surface areas in the two churches with a portable Metrohm (model 827) pH-meter equipped with a flat-membrane electrode (Metrohm, model 6.0256.100). The measurements were made the way that one single drop of electrolyte solution of 3 M KCl (used also inside the electrode) was placed on the surface and the electrode was put onto the drop. The probe was calibrated by the standard procedure with 3 buffer solutions: pH 4: KC₈H₅O₄ (Potassium hydrogen phthalate), pH 7: KH₂PO₄ + Na₂HPO₄ (Potassium dihydrogen phosphate + disodium hydrogen phosphate),

pH 9: H₃BO₃ + Na₂B₄O₇ (Boric acid + sodium tetraborate). The calibration standards were original Metrohm products.

3.4. Ion chromatography of extracts from whitewashed wall surfaces

The fate of the ammonia and other airborne compounds in relation to the chemistry taking place on the surface of the interior walls of the church, was investigated using samples from the walls. Surface areas of ca. 30 × 20 cm were selected inside the two churches (Fig. 2). In Søndersø Church three areas on whitewashed surfaces were selected. The positions of the measurements are shown in Fig. 2a. Similarly three areas of whitewashed surfaces were chosen from Nr. Broby Church; the positions are shown in Fig. 2b.

The ions present in the surface layer of each rectangle were retrieved by washing with deionized water. The water was applied gently along the top of the rectangle by a pre-cleaned squeeze bottle. The water slowly ran down the rectangle and was collected in an apparatus, built in-house, consisting of a funnel made of aluminum foil, which was held tight against the wall, and a small plastic sample bottle (25 mL) for collecting the water. A new funnel and a fresh sample tube were used for each area.

The retrieved water, between 10 and 20 mL, was kept refrigerated until the samples were analyzed on a Metrohm ion chromatograph with modules 818, 819, 820 and 833 equipped with a Metrosep AS5 150/4.0 anion column and AG14 pre-column. The flow was 1.2 mL min⁻¹ of 3.5 mM Na₂CO₃ and 1 mM NaHCO₃. For the cations a Metrosep C4 150/4.0 column was used with the same flow and elute consisting of 1.7 mM HNO₃ and 0.7 mM depicolinic acid. A certified

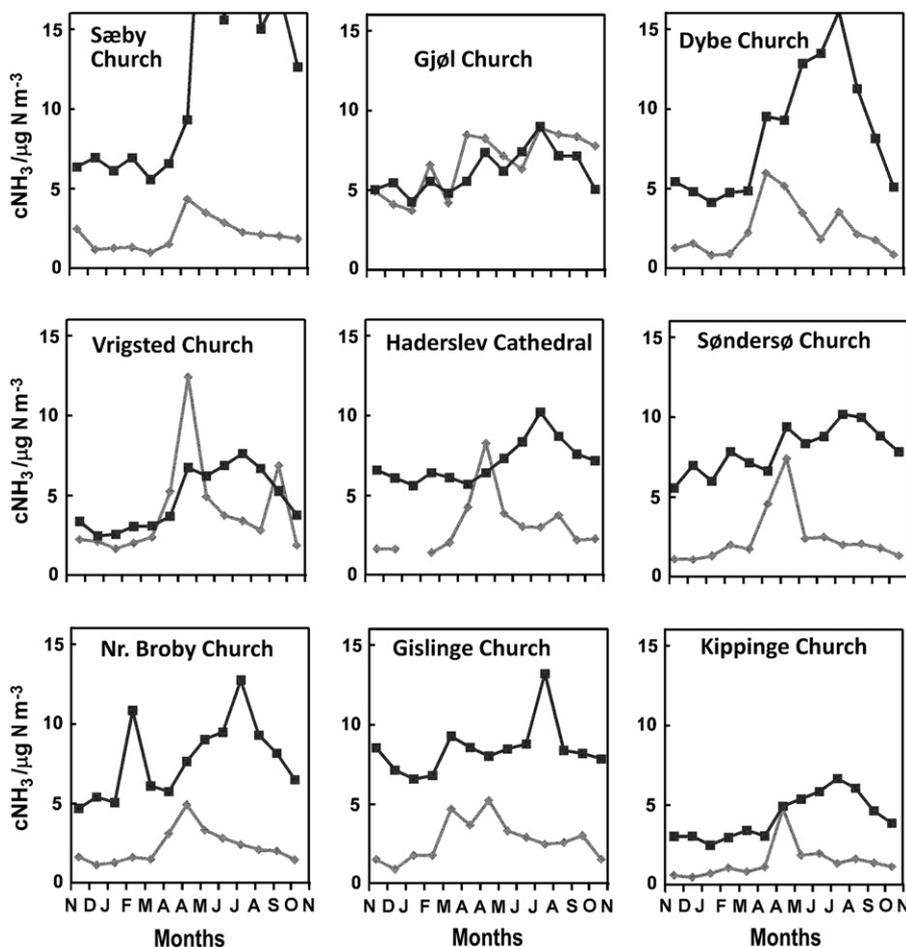


Fig. 3. Concentrations of ammonia during a year (November 2007–November 2008), both indoors (black) and outdoor (gray). The concentration unit is $\mu\text{g NH}_3\text{-N m}^{-3}$. The concentration scale has been set to a maximum 16 for comparability, although this means that some concentrations measured in Sæby church which are as high as $29 \mu\text{g NH}_3\text{-N m}^{-3}$, the result of restoration work, are not shown. The intervals between the changing of the passive samplers varied from 2 weeks to 1 month.

multi-anion standard solution; PRIMUS, from FLUKA Analytical was analyzed also.

3.5. Church practice

A questionnaire was given to the church personnel to record the number of churchgoers, duration of church services, uses of cleaning agents, cleaning routines, and heating and airing policies (see Table 1). The questionnaire was filled out by the church personnel along with any other useful information.

4. Results

4.1. Ammonia measurements at different locations in the church room

Indoor and outdoor ammonia concentrations in the nine churches are shown in Fig. 3. The high concentrations by the end of the year at Sæby are the result of restoration work, where painters used large amounts of ammonia while cleaning the painted and lacquered interior surfaces. All outdoor measurements have peaks in the spring time from April to May, coinciding with the period where spreading of manure is allowed in Denmark. In all the churches except Haderslev Cathedral the indoor measurements exhibit a small peak or a shoulder coinciding with the spring peak outside. Another peak is seen in the indoor measurements in Nr. Broby Church occurring in the period February to March. This early peak is most likely caused by the staff polishing silverware inside the church for a couple of days during this particular measuring period (1 month). However, for all the churches it seems that indoor ammonia concentration is higher than outdoor. In the churches not aired on a daily basis (Table 1) the ratio of indoor to outdoor ammonia concentration is around three. This high ratio is peculiar and raises the question of what the mechanism and consequences can be for the higher indoor ammonia concentrations.

At Nr. Broby a more detailed study used thirty measuring stations the positions of which are shown in Fig. 2b. These were distributed in two rows each consisting of fifteen passive samplers. One line ran east–west along the northern wall and the other line ran parallel to the first line through the center middle of the church. The rationale behind this geometrical pattern was that we wished to investigate if the whitewashed surface acted as a source. The use of a relatively large number of measuring stations was deemed necessary due to a suspicion that local inhomogeneities or systematic differences could occur, e.g. near the entry point at the porch (Danish: *våbenhuset*), near the organ, where air possibly is circulated more vigorously than elsewhere, or that end-effects in either end of the church room could have affected the air circulation. The results of these ammonia measurements at Nr. Broby are shown in Fig. 4.

4.2. Air exchange rates

The air exchange rate measured for Nr. Broby Church varied between 0.09 and 0.24 room volumes h^{-1} , and at Søndersø Church the average air exchange rate was found to be 0.19 room volumes h^{-1} . In Søndersø Church the air exchange rate was also measured during an incident of airing yielding 1.0 h^{-1} . These are rather low air exchange rates compared to the air exchange rates of ordinary houses, where a typical value would be around 0.5 h^{-1} or more. The observed air exchange rates around 0.2 h^{-1} are, however, consistent with measurements made in other similar church buildings by the National Museum of Denmark (unpublished data). It must be expected that the air exchange will vary over the year, depending on weather and the use of the building. However, it may be assumed that the air exchange rate will always be less than 10 church room volumes per day, and mostly less than 5 volumes per day.

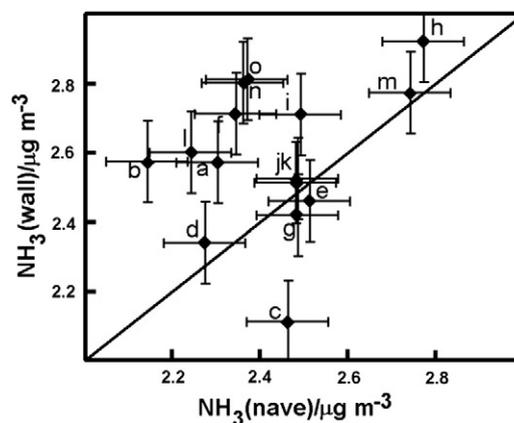


Fig. 4. Comparison of indoor ammonia measurements at the wall as a function of those in the nave of Nr. Broby Church. These are averaged over a time period of 1 day and 21 h when the church was not in use. The measurements made at position a–o are as marked in Fig. 2b. The line shows equal concentration and indicates that in general concentrations close to the wall are higher. The uncertainty is between 0.3 and 9% for the ALPHA measurements, the average being 4%.

4.3. pH measurements

The results of the pH measurements are listed in Table 2. At positions 8 and 9 in Søndersø Church, the pH was first measured on the surface as it was found, and then on nearby surface areas only a few cm away from the original position. However, at these positions the areas were dusted off first with a dry paper tissue. This was done in order to reveal if any acidity was derived from the minute amounts of dust present at the surface. The other surfaces were painted surfaces, a lacquered surface and a granite surface. On one of the painted surfaces (No. 5) and on the lacquered surface (No. 7) measurements were first done on the surfaces as found. Then the surface areas were thoroughly cleaned with a detergent (Deconex) and rinsed in deionized water, this cleaning treatment was repeated 3 times on each area. After drying the pH was measured again. As before this was done in order to monitor if any acidity was present in a surface layer which could be wiped off, which was clearly the case.

Table 2

The pH measurements on selected interior surfaces of Søndersø and Nr. Broby churches. At positions 8 and 9 the measurements were repeated right next to the first measuring position, but on a whitewashed surface dusted off with a dry paper tissue. At positions 5 and 7 the surface area was measured both as found and following a thorough cleaning in detergent (Deconex) and deionized water. The errors quoted are 1 standard deviation calculated on the basis of 3 to 6 repetitions at measuring sites in the immediate vicinity of each other (ca. 5 cm).

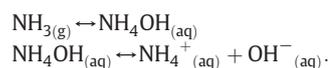
Site	Description	Surface type	pH
Søndersø			
8	Arch in nave	Whitewash	8.57 ± 0.10
8	Arch – dusted surface	Whitewash	8.92 ± 0.05
9	Niche east of arch in nave	Whitewash	7.68 ± 0.12
9	Niche – dusted surface	Whitewash	8.38 ± 0.20
10	Pew	Painted	6.57 ± 0.14
11	Hymn number board	Painted	6.49 ± 0.46
12	Baptismal font	Granite	7.17 ± 0.23
Nr. Broby			
1	Window pane, south	Whitewash	8.67 ± 0.27
2	Arch in nave	Whitewash	7.01 ± 0.74
3	Window pane, west	Whitewash	8.94 ± 0.32
4	Window pane, south	Painted	7.81 ± 0.09
5	Front pew	Painted	6.26 ± 0.05
5	Front pew – cleaned	Painted	8.39 ± 0.10
6	Pew behind organ	Painted	6.01 ± 0.09
7	Communion table	Lacquered	4.52 ± 0.06
7	Communion table – cleaned	Lacquered	6.83 ± 0.08

4.4. Ion chromatographic analyses

The results of the ion chromatograph analyses converted to area concentrations are given in Table 3. Some sample areas exhibited a positive ion balance, *i.e.* with excess cations (LS-1200 and LS-1204), which is probably caused by missing CO_3^{2-} which was not included in the analysis because carbonate was part of the elutant. Three sample areas exhibited an ion balance close to zero (LS-1196, LS-1198, and LS-1206), which is probably because the entire ion inventory was covered by the analyses for these samples. One sample shows a slightly negative ion balance, *i.e.* with an excess of anions (LS-1208). The only viable explanation is the presence of an undetermined cation, amounting to about 7% of the total ion balance. It seems unlikely that substantial amounts of both cations and anions are missing at the same time, so generally speaking there is a good probability that the analyses have detected the majority of anions and cations present in the samples.

4.5. Thermodynamic modeling

The partial pressure of ammonia above a solution can be described in terms of dissolution and dissociation equilibria:



Although the values of these equilibrium constants are well known the ammonium ions present on the church wall are parts of a mixture. At high relative humidity the mixture of ions would be present as a salt solution and as conditions become drier, the solution concentration increases. Once dry the ammonium nitrate salt is also able to decompose to ammonia and nitric acid (Stelson and Seinfeld, 1982); the nitric acid would be absorbed by the alkaline wall. Concentrated solutions behave in non-ideal manner and corrections need to be made for this. Here we have adopted the approach of Pitzer as developed in the AIM Aerosol Thermodynamics Model (Clegg et al., 1992, 1998) and used Inorganic Model III provided online (<http://www.aim.env.uea.ac.uk/aim/aim.php>).

The salt mixtures present on the wall were simplified to reduce the number of calculations and allow for ions that are absent from the model. Such simplifications lead to small errors in the determination of activity coefficients, but will not lead to significant discrepancies in the estimates of ammonia partial pressure. Fig. 5 shows the pressure above a system where the $\text{Na}^+:\text{NH}_4^+$ is maintained at 0.98:0.02 and $\text{Cl}^-:\text{NO}_3^-$ 0.95:0.05. The results of these theoretical calculations show that at high relative humidity and under pH values typically lower than those found on the wall (Table 2) does the ammonia partial pressure fall below 10^{-6} atmospheres (570 $\mu\text{g}(\text{N})$)

Table 3

The concentration ($\mu\text{mol m}^{-2}$) of ions on the walls at Søndersø and Nr. Broby churches. The sample numbers refer to Fig. 2.

	Søndersø			Nr. Broby		
	LS1204	LS1206	LS1208	LS1196	LS1198	LS1200
F^-	0	0	0	1.9	0	0
Cl^-	584	25	1483	248	216	565
Br^-	0	0	0	0	0	0
NO_3^-	1380	22	4586	160	502	661
PO_4^{3-}	0	3.1	0	0	0	0
SO_4^{2-}	257	34	29	5.8	3.8	7.6
Li^+	0	0	27	0.6	0	0
Na^+	2095	2.3	2740	115	120	1037
NH_4^+	0	1.1	72	0.9	0	13
K^+	251	3.7	555	35	65	194
Ca^{2+}	767	140	946	90	266	196
Mg^{2+}	53	9.7	220	0	39	47

m^{-3}) a partial pressure far in excess of that found in the church, so ammonia will degas from the walls under all realistic conditions.

5. Discussion

The simplest interpretation of concentration difference between the center line and the line near the wall suggests that the decay of the ammonium nitrate particles takes place at the walls rather than in the air volume. It supports the notion that ammonia is released as predicted by the thermodynamic modeling. It is possible that this arises from the decay of the ammonium nitrate aerosol particles that have been deposited on the alkaline wall. Parallel results for the particles were reported in urban interiors by Andělová et al. (2010) in the Baroque Library Hall of the National Library in Prague, although the ammonia concentration measurements exhibited a more mixed picture as reported by López-Aparicio et al. (2011). There are also observations that a domestic apartment in Prague showed concentrations where both particles containing NH_4^+ and particles containing NO_3^- are significantly higher in the outdoor air than in the indoor air, but NO_3^- is much depleted (Smolík et al., 2008). These observations are also in line with other studies of the transformations that take place in ammonium nitrate aerosols in the indoor environment, *e.g.* Lunden et al. (2003), although this work takes the view that it is the ammonium nitrate which decomposes in the air and it is nitric acid that deposits to the walls. However, an alternative view might be that the ammonium nitrate particles deposit from the indoor air then the nitric acid transfers to the wall. The former mechanism might be attractive as nitric acid deposition to damp walls might be faster than that of small particles, but the enhancement of indoor ammonia would be much the same as in particle deposition and decomposition.

Outdoor ammonia concentration data from rural Denmark (Andersen and Hovmand, 1994) suggests that the mean ammonia concentrations are typically: NH_4^+ 2.4 $\mu\text{g}(\text{N})\text{m}^{-3}$ and NH_3 1.0 $\mu\text{g}(\text{N})\text{m}^{-3}$. The values estimated for the outdoor ammonia are quite close to the yearly average of values of the measurements outside Søndersø Church (1.70 $\mu\text{g}(\text{N})\text{m}^{-3}$) and Nr. Broby Church (1.64 $\mu\text{g}(\text{N})\text{m}^{-3}$). The total amount of nitrogen associated with the outdoor ammonia in Denmark is thus typically 3.4 $\mu\text{g}(\text{N})\text{m}^{-3}$, which is less than the yearly average measured in the indoor air in this study, Søndersø 7.91 $\mu\text{g}(\text{N})\text{m}^{-3}$ and Nr. Broby 7.89 $\mu\text{g}(\text{N})\text{m}^{-3}$. It may be due to higher yearly averages for outdoor ammonium ions (*i.e.* as ammonium nitrate) at Søndersø and Nr. Broby churches, where nearby agricultural activity could represent an additional source of ammonia. However, this explanation also requires an additional local outdoor source of nitric acid, as rural levels are typically only 0.1 to 0.4 $\mu\text{g}(\text{N})\text{m}^{-3}$ in Northern

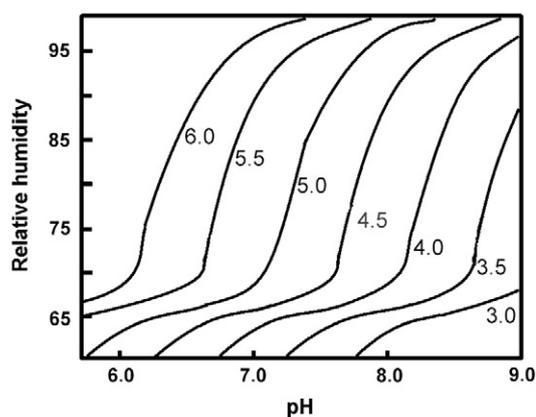


Fig. 5. Predicted ammonia partial pressure above salt solutions ($\text{Na}^+:\text{NH}_4^+$ 0.98:0.02 and $\text{Cl}^-:\text{NO}_3^-$ 0.95:0.05) as a function of pH and relative humidity. The pressures are expressed as the negative logarithm of the ammonia pressure in atmospheres (1 atm = 101,325 Pa).

Europe (Ferm et al., 2005). It is also possible that there were unresolved sources of indoor ammonia. However, typical indoor sources such as flowers, cleaning agents and exhalation from churchgoers (estimated at 0.7 g/year for Nr. Broby) were investigated and appear unlikely to account for the discrepancy. Urea, which is sometimes used for de-icing during the winter, could be carried into churches on shoes and undergo biologically mediated decomposition:



but this mechanism is not supported by high interior ammonia concentrations in winter. Although the excess ammonia cannot be entirely explained it does not alter our conclusions.

If we assume that all the particulate ammonium is present as ammonium nitrate then the amount of nitrate (n_{NO_3}) brought into the church per year is:

$$n_{\text{NO}_3} = c_{\text{air,NO}_3} AC V 24 \times 365$$

where $c_{\text{air,NO}_3}$ is the concentration (ca. $2.4 \mu\text{g(N)}\text{m}^{-3}$), AC is the hourly air change rate, V is the church volume and 24×365 the number of hours in a year. Taking the air change rate from Nr. Broby to be 0.2 h^{-1} and the volume as 1260 m^3 the equation suggests that some 5.3 g or 0.37 mol N are delivered each year. This represents an annual flux of $300 \mu\text{mol m}^{-2}$ for 1553 m^2 of interior surface area. This area estimate includes whitewashed, painted, wooden, granite, and all other surfaces in the room. This is only slightly less than the amount that appears on the church wall (average $440 \mu\text{mol m}^{-2}$ for Nr. Broby Church), which may imply that this excess nitrate is abraded from the walls on a roughly annual time scale or that the walls of Nr. Broby Church was cleaned ca. a year prior to our sampling. For Søndersø the church volume is 1680 m^3 and the entire interior surface area ca. 1643 m^2 , which leads to a calculated yearly flux of $310 \mu\text{mol m}^{-2}$. Here there is approximately $2000 \mu\text{mol m}^{-2}$ found on the walls at Søndersø (from Table 3), which would thus require perhaps 7 years to accumulate and hints at a longer residence time on the walls. This accumulation of this amount of nitrate is not unreasonable given that the murals were last restored in 1933.

High indoor concentrations of ammonia imply a flux of ammonia to the outdoors. As this ammonia arises from the walls it implies a loss of alkalinity.

$$n_{\text{NH}_3} = c_{\text{air,NH}_3} AC V 24 \times 365$$

where $\Delta c_{\text{air,NH}_3}$ is the difference between the indoor and outdoor concentrations taken to be $6.2 \mu\text{g(N)}\text{m}^{-3}$ at Søndersø, which suggests that some 0.98 mol of acidity is created on the walls each year with the conversion to half this amount of calcium carbonate to soluble salts on the wall each year (2 mol of HNO_3 react with each mol CaCO_3). However, spread over the entire wall this would amount to $300 \mu\text{mol m}^{-2}$, which is close to the measured values on the church wall $140\text{--}950 \mu\text{mol m}^{-2}$. This estimated annual and measured deposit represents $0.03 \text{ g}(\text{CaCO}_3)\text{m}^{-2}$ or a layer of calcium carbonate (density 2.7 g cm^{-3}) only a micron thick layer each century. The rate might be twice this amount if all the deposit occurred solely to lime washed surfaces. Even so, this acid attack seems not to represent a substantial rate of damage that would be capable of inflicting deterioration to the murals even over several centuries. However, it may play a role in the damage of the murals in an indirect way. The major path of mural deterioration in the Danish churches is due to salt damages, which was accelerated by the onset of heating (unfriendly heating) initiated in the early or mid 1800s and maintained even till this day. The major source of humidity on walls and vaults is leaking roofs. With the onset of heating followed evaporation on the inner surface of the walls and vaults, and this led to an increase of the concentration of salts on the interior surfaces.

The accumulation of calcium nitrate is supported by the inventory of soluble ions on the walls. It is not a straight forward matter to define the source(s) of the ions. However, the data (Table 3) exhibits some characteristic features. The concentrations of the Na^+ and the Cl^- balance at an average of about 25% each, by balance is meant the lowest number of ($[\text{Na}]$, $[\text{Cl}]$), which suggests a source as NaCl . Two obvious possibilities are capillary transport of ground water to the walls or deposition of airborne sea-salt particles, ubiquitous anywhere in Denmark. We lean toward the latter explanation. The nitrate anion makes about 50% of the inventory often balanced by Ca^{2+} and to a lesser degree Mg^{2+} . These elements are of course present in excess in a lime washed wall. It is therefore a likely explanation that the NO_3^- arrived to the wall as HNO_3 , which was neutralized on the lime wash leaving only the NO_3^- .

The acidity of the indoor lime washed surfaces is as expected in the pH range of 7.8 to 8.8 reflecting the action of the alkaline carbonate. The acidity of the non-reactive interior surfaces like paint, lacquer and stone surfaces have generally lower pH than 7, the lowest being 4.5. These pH measurements are best explained by the accumulation of acids on the interior surfaces. When the surfaces are washed and subsequently measured the pH values are higher than the original measurements suggesting that the deposited acid has been removed.

6. Conclusion

Ammonia chemistry on the walls of the church enhances the ammonia concentrations indoors. This seems to involve the conversion of ammonium nitrate to ammonia which may volatilize from the alkaline walls, a mechanism that has also been argued as a source of ammonia in other urban interiors. There is a slight excess of ammonia (about two times the expectations) within the church compared with ammoniacal nitrogen in the incoming air. Indoor sources such as floral arrangements, cleaning agents and other human activities seem too small, which may imply the possibility of local sources for outdoor ammonium nitrate aerosol. There is a need for future work to explore the higher than expected loadings of ammonium nitrate in these rural locations.

The loss of ammonia from the incoming ammonium nitrate increases the acidity on the interior surfaces. So in addition to ammonia being a possible agent of damage due to enhancement of fungi growth, nitric acid originating from the oxidation of NO_x from combustion processes contributes to the formation of calcium nitrate on walls. There is the potential for nitrate concentrations in the 20th century to degrade the murals of the rural churches. This nitrate could arise as nitric acid (combustion) or ammonium nitrate (when combined with ammonia emissions from farming); both the volume of farming and traffic have increased significantly in Denmark over the last century. Even though an acid deposition may harm some objects, such as lime-wash, metal and polychrome, the quantities of calcium nitrate found on the interior walls are relatively small and probably insufficient to cause deterioration of the murals due to direct acid attack even over several centuries. Salt weathering typically involves larger amounts of salt in association with crystalline efflorescence. Calcium nitrate crystals (known as *wall saltpeeter*) are frequently found on old walls, but these are derived from contact with dung or more commonly bird droppings on top of the vaults, not the mechanism suggested here. It is possible that calcium nitrate, which is very hygroscopic, maintains a water film on the wall. This could enhance deposition of pollutants to the wall, but as we argue above the quantities remain small.

It could be that ammonia rather than the nitric acid remains responsible for harmful effects through promoting biological growth, discoloring the pigments or reducing the cohesiveness of the plaster. However, little ammonium is found on the walls in this study. It is important to consider that murals, once uncovered, are exposed to church heating and a wide variety of threats, such as sea salts, so

although the potential risks are easy to attribute, it is much more difficult to isolate a single specific culprit.

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Appendix A. Supplementary data

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