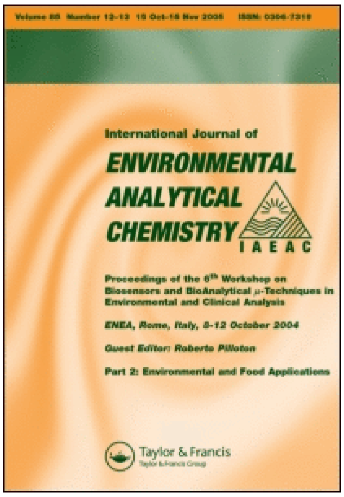


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Characterization of Indoor Air Quality in the Church of San luigi Dei Francesi, Rome, Italy

F. De Santis[a]; I. Allegrini[a]; M. C. Fazio[a]; D. Pasella[a]
[a] CNR—Istituto Inquinamento Atmosferico, A. d. R. Roma, Monterotondo Scalo, Roma, Italy

To cite this Article De Santis, F. , Allegrini, I. , Fazio, M. C. and Pasella, D.(1996) 'Characterization of Indoor Air Quality in the Church of San luigi Dei Francesi, Rome, Italy', International Journal of Environmental Analytical Chemistry, 64: 1, 71 — 81

To link to this Article: DOI: 10.1080/03067319608028336
URL: http://dx.doi.org/10.1080/03067319608028336

Intern. J. Environ. Anal. Chem., Vol. 64, pp. 71–81
Reprints available directly from the publisher
Photocopying permitted by license only

CHARACTERIZATION OF INDOOR AIR QUALITY IN THE CHURCH OF SAN LUIGI DEI FRANCESI, ROME, ITALY

F. DE SANTIS, I. ALLEGRINI, M. C. FAZIO and D. PASELLA

CNR—Istituto Inquinamento Atmosferico, A. d. R. Roma, Via Salaria Km 29,300, CP 10, 00016 Monterotondo Scalo, Roma, Italy

(Received, 20 October 1995; in final form, 5 March 1996)

Simultaneous indoor and outdoor samples collected in the Church of San Luigi dei Francesi were analyzed for nitrous acid, sulphur dioxide, nitrogen oxides and ammonia in the gas phase and for ammonium, sulphate, and nitrate ions in the particulate matter. Indoor levels of nitrogen oxide, nitrous acid and ammonia were found to largely exceed those outdoors. For NO_2 and SO_2 lower indoor levels were always measured, while for nitrate and sulphate, the indoor/outdoor ratios ranged from 0.5 to 3.5. These results show that indoor production of nitrous acid could result from heterogeneous reactions indoors, on the walls and exposed surfaces. Furthermore, they demonstrate that non-reactive species such as nitrogen oxide and particles penetrate indoors, where they remain segregated and are very slowly depleted, due to their small deposition velocities.

KEY WORDS: Indoor pollution, diffusion techniques, nitrous acid, nitric acid

INTRODUCTION

A factor which is often overlooked in the confined environment of a building intended for storing or displaying artworks or manufacts of cultural or artistic value, is the role of atmospheric pollutants which can be transferred indoors. In this regard, it is known that an important process which contributes to the damage of artworks is the dry deposition of acidic species[1–3] and ozone[4]. Acidity in the air is essentially caused by criteria pollutants, such as sulphur and nitrogen oxides, which are emitted into the atmosphere by sources related to industry, transportation and heating. These species are transformed in the atmosphere, through complex reaction pathways, into secondary pollutants, in particular into gaseous nitric and nitrous acids and into acidic sulphates in particulate matter. A recent study of the air quality in one of the most important Italian Museums—the Uffizi Gallery, Florence—has demonstrated the presence of consistent levels of HNO_3 and other aggressive species such as SO_2 and O_3[5] which have been ascribed to penetration from outdoors. In the same study, high levels of indoor HONO, greatly exceeding those outdoors, have also been measured. Although the exact mechanism of formation of this species is still not completely understood, there are sound indications[6–8] that its presence indoors could be indicative of a major hazard to the artworks in consideration of the fact that HONO production is coupled with the heterogeneous formation of HNO_3 on surfaces- most likely including artworks-according to the following reaction:

$$2\,NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad (1)$$

Laboratory studies[6] have clearly shown that HONO produced and adsorbed on the surfaces is released in the gas phase while HNO_3 tends to remain adsorbed on the surfaces. The distribution of the reaction products of reaction above on a pyrex glass surface was that more than 98% of nitrous acid was released in the gaseous phase while HNO_3 was entirely retained on the glass walls of the reactor.

This paper reports the observations and analysis of some of the mentioned primary and secondary pollutants in the church of San Luigi dei Francesi in Rome. The sampling has been carried out in the Contarelli Chapel where three famous paintings of Caravaggio, painted between 1597 and 1602 (St. Matthew and the Angel, the Calling of Matthew and the Martyrdom of St. Matthew), are displayed.

In consideration of the value and importance of these masterpieces, this church, besides being a place of worship, can be regarded as a museum. As such, the Contarelli Chapel is visited by hundreds of tourists every day.

The objective of the present study was to compare the concentration of some criteria and non-criteria air pollutants inside the church and their relationship with the concentration outside. This has been done during the cold season when domestic heating in the city adds to traffic as a source of emission and thermal inversions accumulate pollutants at ground level.

EXPERIMENTAL

The reported measurements were made in the church of San Luigi dei Francesi in Rome during the period 10–15 February 1995. The church which is large and richly decorated, is an outstanding example of the late Renaissance style. The sampling has been carried out in the Contarelli Chapel which is located in the left aisle near the apse, opposite the main entrance.

In order to investigate the indoor/outdoor relationships as well as the quality of indoor air in the church, the following equipment has been employed:

- Two sampler units equipped with annular denuders for the collection of HONO, SO_2, NO_2, NH_3 and particulate matter, one placed in the Contarelli Chapel and the other outdoors in the courtyard of the church.
- NO and total oxidized nitrogen NO_X concentrations were continuously measured using a chemiluminescence analyzer (Environment AC30). A single instrument was used to alternate sampling between indoors and outdoors by means of a three-port Teflon solenoid valve on a 10 min cycle.

The sampling procedure based on annular denuders for the simultaneous determination of HONO, SO_2, NO_2 and particulate matter developed earlier in our laboratory[9,10] has been adopted for this study. To this end, annular denuders (i.d. = 30 mm, o.d. = 33 mm, length 220 mm) at a sampling flow rate of 1 l min^{-1} were used. The sampling lines were composed of a train of five annular denuders (1 TCM coated for SO_2 followed by 2 Na_2CO_3 coated for collecting HONO, 1 citric acid coated for NH_3 and 1 carbon coated far NO_2) and a triple filter pack. The filter pack which contained a Teflon filter followed by a nylon and a citric acid impregnated filter, was preceded by a cyclone that removed particles larger than 2.5 μm. The novelty of the present set-up was the use of a fifth denuder coated with citric acid for the collection of NH_3. A series of experimental trials carried out in the laboratory by using a source of NH_3 under conditions representative of those encountered in the field, has shown that the recovery of this species is not affected by the TCM and Na_2CO_3 coatings[11]. After sampling, the Na_2CO_3 and carbon coated denuders were extracted with 10 ml of distilled water and the extracts analyzed for anions by ion chromatography (Dionex, Model DX500). The TCM and citric denuders were also extracted with 10 ml of distilled water and then analyzed spectrophotometrically by pararosaniline and indophenol methods, respectively. The analysis of the filters was carried out by ion chromatography after extraction with 10 ml of the Dionex eluent for 20 min in ultrasonic bath.

In consideration of the time of the year when the measurements were carried out (mid February) the concentration of O_3, whose aggressive properties towards artworks are well known[4], was not measured since its indoor concentration tends to be insignificant due to a negligible photochemical activity outdoors. In addition to this, the location where the measurement campaign was carried out (downtown Rome), is characterized by a high level of NO (typically 400–600 $\mu g\ m^{-3}$). The gas phase reaction

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad [2]$$

is very tast as evidenced by its second order rate constant of $4.4 \times 10^{-4}\ ppb^{-1}\ s^{-1}$ at 25°C. On this basis, it is clear that significant concentrations of O_3 can only occur when little NO is present.

As far as HNO_3 is concerned, it is known that significant concentration levels of this species can occur indoors only during the summer (essentially due to infiltration from outdoors[3] and also to the indoor reaction between O_3 and NO_2[12]). Therefore, this species was not measured on a regular basis. However, since we were seeking a confirmation to a mechanism of production of HONO which entails an equimolecular production of HNO_3 (reaction [1]), on Feb. 15 and 16 a second denuder line for the measurement of HNO_3 according to Perrino *et al.*[13] (composed of two NaCl coated denuders placed in line) was set-up. The measured concentrations of HNO_3 (lower than 10.3 $\mu g\ m^{-3}$) is negligible and lends support to the findings[3,6] that the reaction product HNO_3 produced through reaction [1] is not released to the atmosphere. Apparently, although equation [1] produces both HONO and HNO_3, *only* HONO is released in the atmosphere while HNO_3 remains adsorbed on the reactive surfaces.

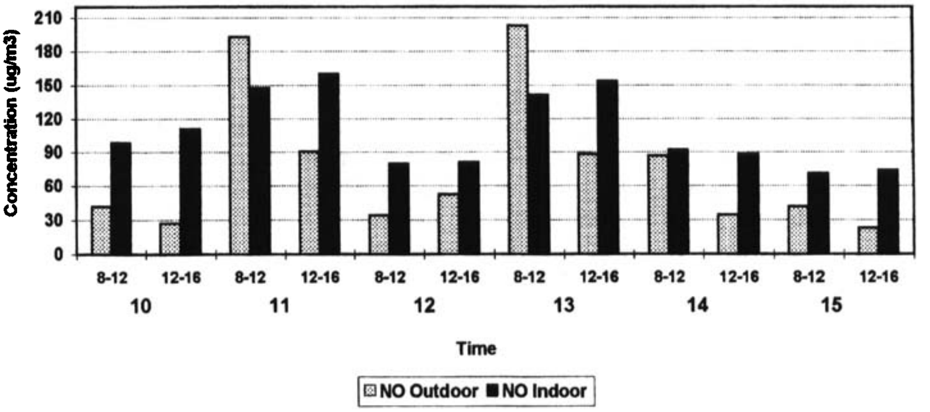
NO_X was measured continuously during the opening hours of the church, from 8 a.m. till 4 p.m., while the other pollutants were measured during two consecutive 4-hour periods from 8 a.m. to 12 a.m. and from 12 a.m. to 4 p.m..

RESULTS AND DISCUSSION

Figure 1 displays indoor and outdoor concentrations of NO and NO_2 as measured by the chemiluminescence technique for the 6-day period under study. To be consistent with the figures for NO_2 and the other pollutants which refer to the annular denuder measurements (which will be presented later) we have reported the data averaged over subsequent 4-hour periods. It is interesting to note that the concentration levels of NO are always much higher indoors with the only exception for the periods 8 a.m.–12 a.m. of Feb. 11 and 13 while for NO_2, as expected, the indoor levels are constantly lower than outdoors.

The outdoor NO concentrations follow a typical pattern with high levels during the morning (due to rush-hour) and lower levels in the early afternoon.

Nitric oxide is the main nitrogen species emitted as a result of combustion processes. This species is not removed from the atmosphere very effectively through the mechanism of dry deposition. In the open atmosphere it is quickly oxidised (mainly by ozone) to nitrogen dioxide and, eventually, to nitric acid and nitrate aerosol. In the confined environment of the church, these oxidation reactions are slow because they are limited by the availability of the oxidants and the extent to which the reaction with ozone controls the rate of removal of NO is essentially determined by the amount of ozone which is present indoors. Since the majority of the ozone in the troposphere is



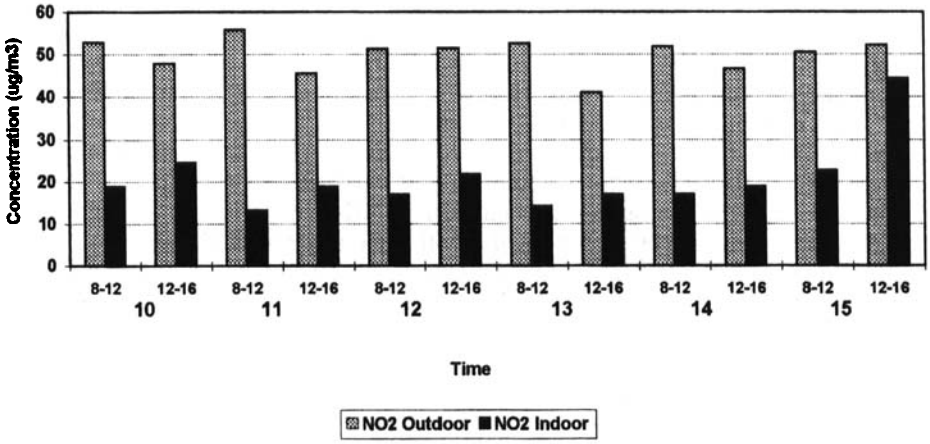


Figure 1 Concentration of NO and NO_2 measured by chemiluminescence technique for the San Luigi dei Francesi Church, Rome, 10–15 February, 1995.

formed by the action of sunlight on nitrogen dioxide, in winter its formation is minimal. In the closed environment of the church, the exchange rate is a key parameter which represents a major factor in determining indoor concentrations and the time availability for indoor reactions. No estimates of the exchange rate have been made in this study. However, due to the peculiar characteristics of the church (few high windows, permanently closed during the measurement campaign) and since the opening of the door was the only cause of infiltration for the outdoor air, this parameter must be extremely low. Consequently, when a pollutant is transferred indoors it can be removed only thanks to its reactivity.

Figure 1 is a clear example of this behaviour. The level of indoor NO, a species which is characterized by a very low deposition velocity, is normally much higher than the level of NO outdoors. Evidently, once this species is transferred indoors, in particular during not uncommon pollution episodes that occur outdoors especially during winter, it becomes segregated and remains indoors being depleted very slowly due to its small deposition velocity. It is interesting to note that during some day characterized by relatively clean air (e.g. on Feb. 10, 12, 14 in the afternoon and on Feb. 15) the concentration of indoor NO continues to remain high. Furthermore, due to the extremely low exchange rate, the shallow NO indoor maxima on Feb. 11 and Feb. 13 lag the corresponding outdoor maxima by as much as about 4 hours (Figure 2). In consideration of the low reactivity of NO, this species can be regarded as a "tracer" for the evaluation of the penetration of outdoors air. A simple calculation on the basis of the measured lag for NO and of the geometry of the church yields an average wind speed of 0.05 m sec^{-1} which is in agreement with air velocities measured in residential indoor environments[14].

The variability of the NO concentrations observed outdoors can be explained on the basis of the traffic and meteorological conditions. As an example, on Feb. 12, a Sunday, the autovehicular traffic was strongly reduced, thus leading to a low level of NO concentration. Low concentrations were also measured on Feb. 14 and 15. In this case the traffic was heavy as usual but intense rain caused a low concentration level of NO.

Figure 3 displays indoor and outdoor concentrations of SO_2, NO_2, HONO, NH_3, respectively as measured by the annular denuder technique for the 6-day period under investigation. The figure shows that the concentration levels of HONO, and NH_3 are

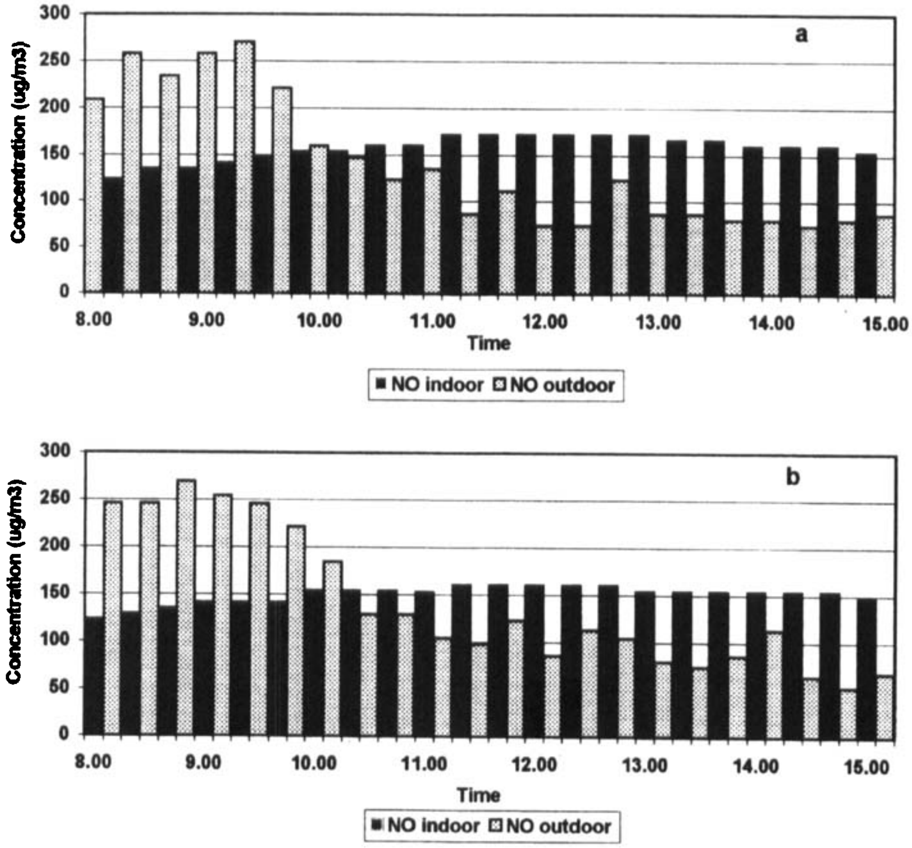


Figure 2 Measured indoor-outdoor NO levels for the San Luigi dei Francesi Church, Rome, on February 11 (a) and February 13 (b), 1995.

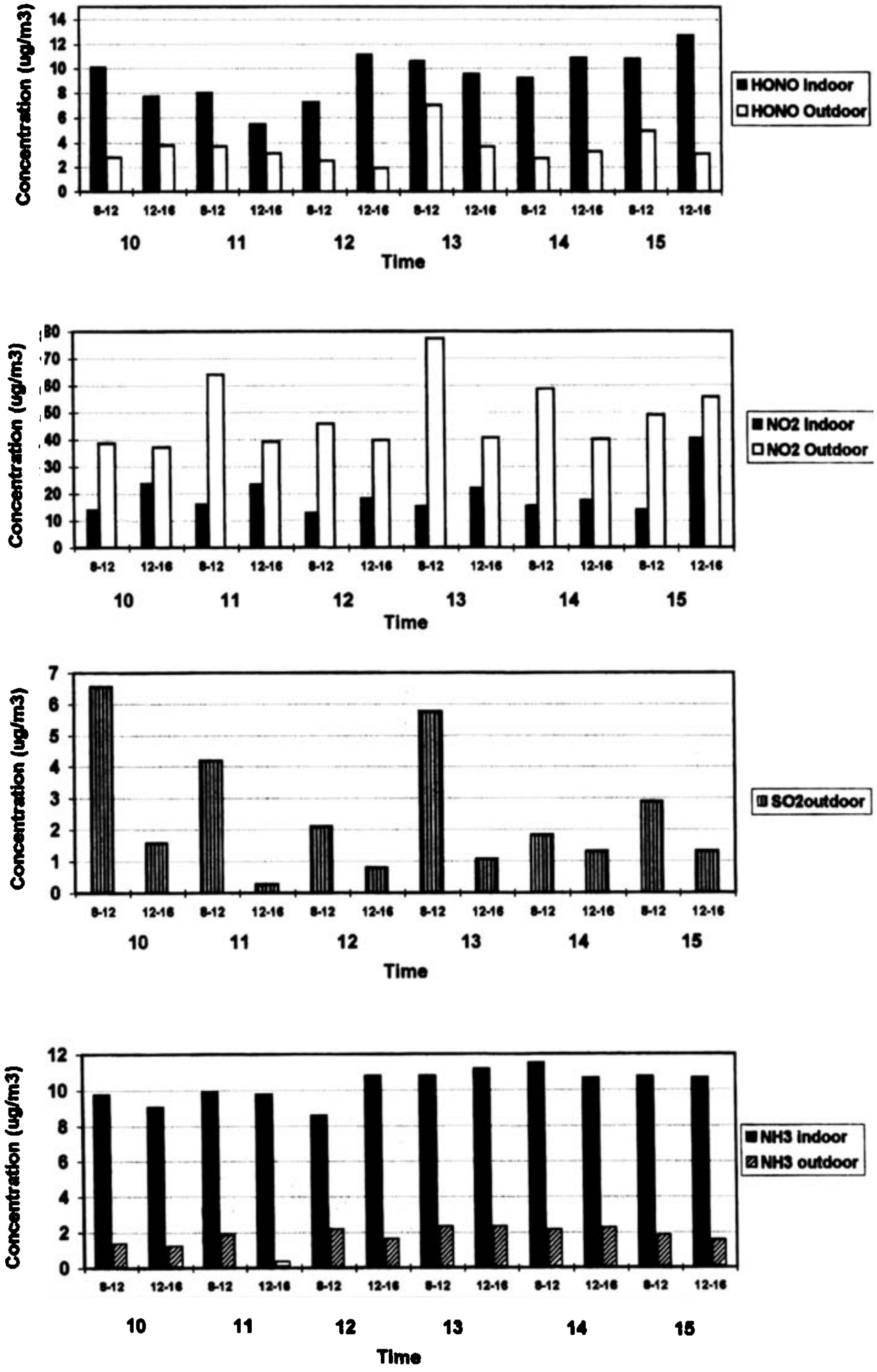


Figure 3 Concentration of HONO, NO_2, SO_2 and NH_3 measured by the denuder technique for the San Luigi dei Francesi Church, Rome, 10–15 February, 1995.

always higher indoors while for NO_2, as already observed with the chemiluminescence technique, the indoor level is lower than outdoors. In the case of SO_2, outdoor concentrations ranged from 1 $\mu g\ m^{-3}$ to 6 $\mu g\ m^{-3}$ while the corresponding indoor values were always below the minimum detectable level for this determination (less than 0.2 $\mu g\ m^{-3}$). This is not a surprising result based on the high deposition velocity of SO_2. Figure 3 also displays the mixing ratios of HONO during the period under study.

By itself, nitrous acid is only slightly acidic and, though a specific study on the effect on surfaces has not been done yet, it is likely that it does not have, as such, any major effect on the exhibits. Previous investigations on indoor HONO have shown that formation reactions in homogeneous phase are of negligible importance e.g.[6,16] and that a likely source of nitrous acid is the heterogeneous reaction [1][6-8]. Therefore, the presence of nitrous acid in the indoor air of the church could be of high importance because this is an indication of the concurrent formation of nitric acid according to the reaction above on the surfaces. It is interesting to note that when HONO is produced on a surface it can react with the substrate or can be released in the atmosphere as a function of the acid-base characteristics of the surface whereas HNO_3, which is much more reactive, tends to "stick" to the surface. As a consequence, although HNO_3 is formed in equimolecular amount according to reaction [1], its indoor concentration is much lower than that of HONO. It is also worth noting that since indoor environments are characterized by high surface to volume ratios in comparison to those outdoors, the formation of nitrous acid is favoured in these conditions. Furthermore, the photolysis of HONO to yield NO and OH radicals which contributes to maintain the concentration of this outdoor species at a low level, is hindered in this indoor environment.

Assuming an average concentration of NO_2 of 28 $\mu g\ m^{-3}$, a surface/volume ratio of 0.7 and using two different values of formation constants for HONO of 6×10^{-6} m s^{-1} (from reference 6) on pyrex glass and of 5×10^{-5} m s^{-1} (from reference 17) on a porous material like nylon, the formation rates of HONO are calculated to be 0.4 $\mu g\ h^{-1}$ and 3.8 $\mu g\ h^{-1}$, respectively. These values underestimate the experimental concentration values measured in this study. Performing a reverse calculation on the experimental data a surface formation constant of 5×10^{-4} m s^{-1} which is an order of magnitude greater than that of nylon can be found. This indicates that the complex nature of the actual surfaces present in the church (consisting of wood, marbles, plaster, textiles, paintings etc.) can not be simplified by resorting to simple laboratory studies on a specific surface. Figure 3 also presents the results of the NH_3 determination in gas phase. The indoor values are consistently higher than those outdoors. It is well-known that ammonia is the most important neutralising compound in the atmosphere. Its major sources in the urban area under consideration, include animal wastes, industrial emission, and traffic. A contribution indoors, besides transport from outdoors, arises from human respiration. On this basis, one may argue that the contribution of this indoor source would had been particularly high on Sunday when the celebration of the Mass (at 10.30 a.m.) entails a remarkable presence of people. Nevertheless, from the data it is apparent that only a modest increase in the concentration of NH_3 occurred later during the afternoon.

Unfortunately, the time resolution used (4 hours) makes the interpretation difficult. The presence of this species in the church can be considered, in an over-simplified way, as beneficial in consideration of its buffer capability towards acidic species such as nitric acid, SO_2 or acidic particulate matter. However, it should be stressed that our knowledge of the mechanisms of deposition of gases and particles is so incomplete, and recognition of the complexities of dry deposition is so recent, that an accurate assessment of the presence of this species in an indoor environment is difficult.

Since indoor NO_2 was measured by two different methods (i.e. the recently developed carbon denuder method and by chemiluminescence) a comparison has been carried out.

In this regard, it is known that the chemiluminescence technique is not specific for the determination of NO_2. In fact, this technique is not able to distinguish NO_2 from other secondary nitrogenous species such as HONO, HNO_3 and peroxyacetylnitrate (PAN)[18,19]. In particular it has been shown$_6$ that the positive interference of HONO, the main nitrogenous species which can affect the measurement, with the type of converter (molybdenum) used in the analyser employed in the present investigation, is 100%. Therefore, a meaningful comparison between methods should be made, taking into consideration the data obtained from the chemiluminescence analyses and the sum of NO_2 + HONO found by using the denuder technique. In order to be consistent with the denuder measurements which were expressed for 4 h periods, the chemiluminescence values for NO_2 are an average of 12 separate determinations.

The result of this comparison has been reported in Figure 4. A reasonable agreement with occasional noticeable differences between the techniques can be observed. The regression analysis made on the chemiluminescence results against the denuder results gives a slope of 0.93 and a correlation of $r^2 = 0.82$. This field intercomparison, though based on few data, indicates generally lower results for the chemiluminescence method. The reason for this discrepancy could not be identified. Since outdoor and indoor air was sampled using a Teflon tubing about 7 m long, we investigated a possible negative artefact on the sampling efficiency of HONO due to the relatively high residence time of HONO in the tubing before sampling. This was done in laboratory by alternate sampling, a source of HONO, prepared according to Febo and Perrino[6], with the chemiluminescence analyzer through a short tubing of Teflon and a 7 m coil of the same material. No sensible effect on the collection efficiency was found.

As far as particulate matter is concerned, its concentration indoors is expected to depend on transport from outdoors and also on the presence of people. A visual comparison of the blackness of the spot produced on the Teflon filters used for the collection of particulate matter, demonstrates that the concentration of the carbonaceous material is much higher indoors than outdoors. It is well-known that particles of an aerodynamic diameter greater than 2.5 μm are described as coarse particles and those of less than 2.5 μm are fine particles. Coarse materials are those usually derived from the earth's crust such as soil dust, sea spray or from dust releases from roads and industrial activities. Fine particles comprise secondarily formed aerosols, combustion particles and

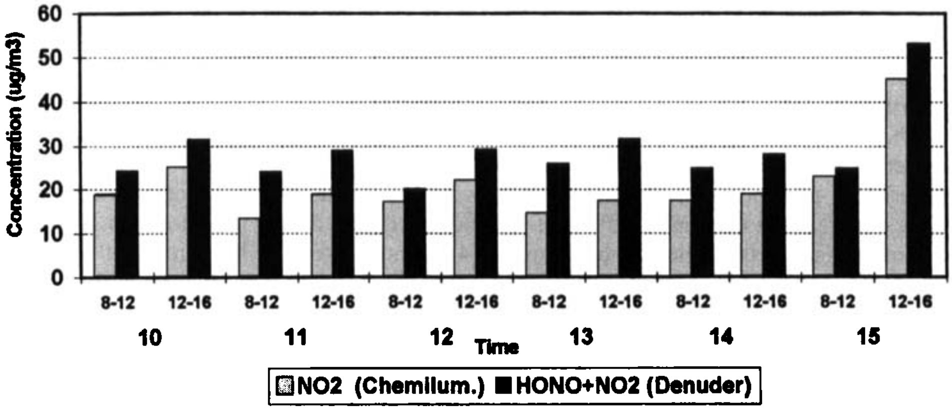


Figure 4 Comparison of indoor NO_2 measured by chemiluminescence and by the denuder technique for the San Luigi dei Francesi Church, Rome, 10–15 February, 1995.

recondensed organic vapours. The acid component of particulate matter generally occurs as fine particles, this is the reason why a cyclone with cut-point at 2.5 μm has been adopted in the present study. Coarse particles have high settling speeds which results in relatively short atmospheric lifetimes. On the contrary, fine particles in the range 0.2–2.5 μm have a much longer atmospheric lifetime (7–30 days), whilst the finest particles which are < 0.2 μm, have a very short lifetime as they regularly coagulate into larger particles.

Even if some forms of worship (such as the lighting of candles or oil lamps and burning of incense) could play a role it seems much more probable that high concentration levels of carbonaceous matter occur indoors as a consequence of the same transport mechanisms invoked for explaining the high levels of NO (i.e. transport indoors during pollution episodes and then slow depletion due to the small deposition velocity). Figure 5 displays indoor and outdoor concentrations of nitrate, sulphate, and

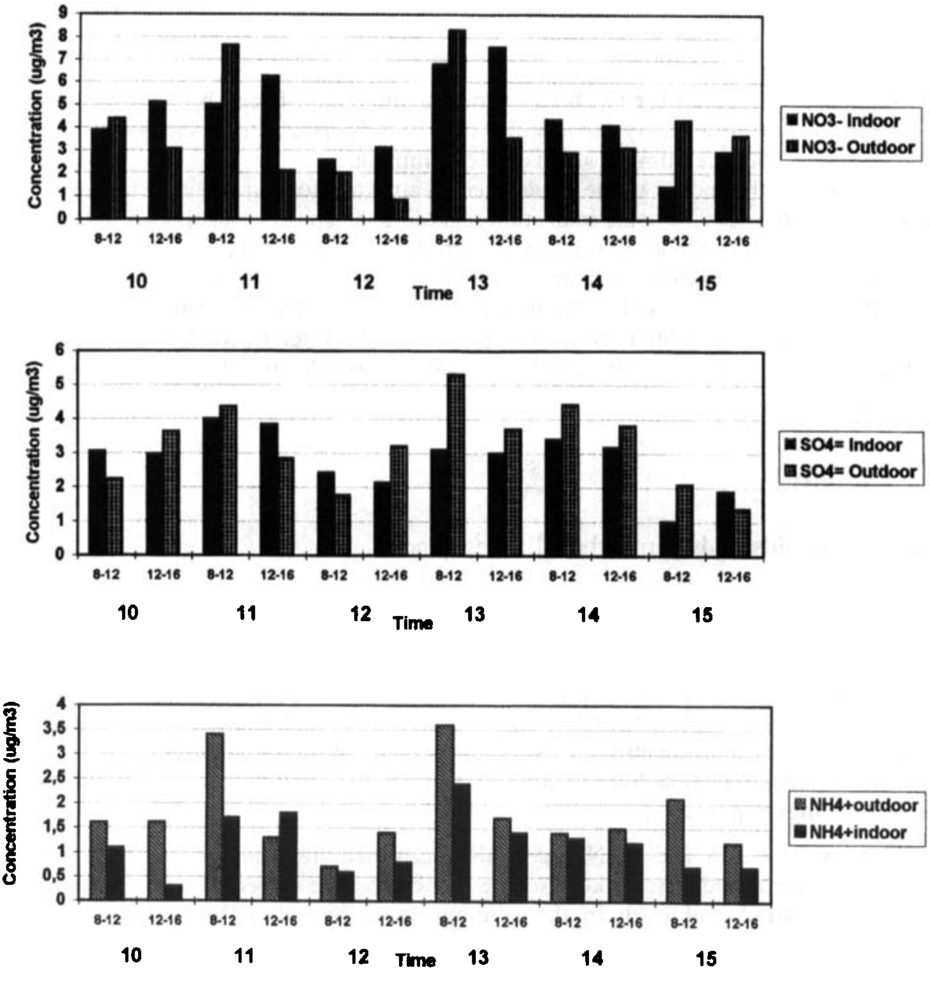


Figure 5 Measured indoor-outdoor nitrate, sulfate and ammonium concentrations for the San Luigi dei Francesi Church, Rome, 10–15 February, 1995.

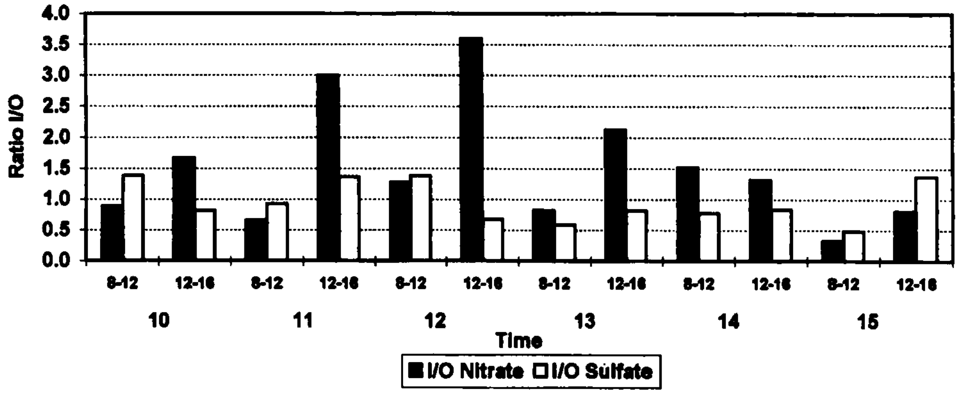


Figure 6 Measured indoor-outdoor ratios for nitrate and sulfate for the San Luigi dei Francesi Church, Rome, 10–15 February, 1995.

ammonium as measured for the 6-day period under study. It can be noted that indoor concentrations follow fairly closely the trend outdoors and that there is consistent correspondence between timing of maxima and minima.

The ratios of the indoor to the outdoor concentrations for nitrates and sulphates have been examined to provide some indication regarding the sources and sinks of the species. The church indoor/outdoor (I/O) ratios for nitrates (Figure 6) which are highly variable and almost always higher than unity, are consistent with a mechanism whereby air infiltration from outdoors is not the major determinant of the concentration indoors. In the case of sulphates, which are largely present in the finer fraction of the particulate matter, and which more easily penetrate inside the church, the I/O ratio is much more constant and near unity.

CONCLUSIONS

The results of this study permit the following conclusions:

- Gaseous species and particles are transferred inside where they reach an equilibrium or a final sink. The extent to which these two processes occur dominantly depends on chemical reactivity and on a multiplicity of factors, such as temperature and relative humidity that interact in complex ways. Non-reactive species such as NO and carbonaceous particles, which are slowly removed by dry deposition, accumulate indoors and reach concentration levels higher than outdoors. On the contrary, a highly reactive species such as SO_2, is quickly removed on the surfaces, possibly including the paintings exposed.
- High levels of NH_3 and HONO have also been measured indoors. For NH_3, besides transport from outdoors, a likely source is the presence of people who gather before the Contarelli Chapel to admire the paintings. In the case of HONO, a likely source of this species could be the reaction of NO_2 and H_2O in heterogeneous phase which produces a stoichiometrically equivalent amount of HNO_3. If this heterogeneous mechanism were predominantly active, the presence of nitrous acid could be a cause for concern with regard to the preservation of the paintings.

Acknowledgments

The authors are grateful to Mgr. J. Madelin and to Mr. P. Mercier of the San Luigi dei Francesi Church for their kind interest in this work. Thanks are due to P. Muthusubramanian for helpful discussions. The financial support of the Commission of the European Communities under the Environment Program EV 5V-CT94-0537 and of CNR under the Progetto Strategico Beni Culturali, is gratefully acknowledged. We are indebted to Mr. M. Montagnoli for his assistance in the measurement campaign.

References

1. N. S. Baer and P. N. Banks, *Int. J. Museum Management Curatorship*, **4**, 9–20 (1985).
2. P. Brimblecombe, *Atmos. Environ.*, **24B**, 1-8 (1990).
3. M. W. M. Hisham and D. Grosjean, *Environ Sci. Technol.*, **25**, 857–862 (1991).
4. D. Grosjean, P. M. Whitmore, G. R. Cass and J. R. Druzik, *Environ. Sci Technol.* **23**, 1164–1167 (1989).
5. F. De Santis, V. Di Palo and I. Allegrini, *Sci. Total Environ.*, **127**, 211–223 (1992).
6. A. Febo and C. Perrino, *Atmos. Environ.* **25A**, 1055–1061 (1991).
7. A. Febo, F. De Santis, C. Perrino and A. Liberti, In: *Proceedings of Tropospheric NO_x Chemistry-Gas Phase and Multiphase Aspects* (O. J. Nielsen and R. A. Cox, Eds.), Roskilde, 1987 pp. 61–67.
8. M. E. Jenkin, R. A. Cox and D. J. Williams, *Atmos. Environ.*, **22**, 487–498 (1988).
9. I. Allegrini, F. De Santis, V. Di Palo, A. Febo, C. Perrino, M. Possanzini and A. Liberti, *Sci. Total Environ.*, **67**, 1-16, (1987).
10. F. De Santis, P. Di Filippo and I. Allegrini, *Proceedings of the 2nd Int. Conference on Air Pollution*, (Brebbia et al., Eds, Barcelona 26–30 Sept., 1994) pp. 425–432.
11. C. Perrino, unpublished results.
12. C. J. Weschler, M. Brauer and P. Koutrakis, *Environ. Sci. Technol.*, **26**, 179–184 (1992).
13. C. Perrino, F. De Santis and A. Febo, *Atmos. Environ.*, **24A**, 617–626 (1990).
14. T. G. Mattews, C. V. Thompson, D. L. Wilson, A. R. Hawthorne and D. T. Mage, *Environ. Internat.*, **15**, 545–550 (1989).
15. E. W. Kaiser and C. H. Wu, *J. Phys. Chem.*, **81**, 1701-1706 (1977).
16. G. W. Harris, W. P. L. Carter, A. M. Winer, J. N. Pitts Jr., U. Platt and D. Perner, *Environ. Sci. Technol.*, **16**, 414–419 (1982).
17. C. Perrino, F. De Santis and A. Febo, *Atmos. Environ.*, **22**, 1925–1930 (1988).
18. C. W. Spicer, D. V. Kenny, G. F. Ward, I. H. Billick and N. P. Leslie, *Air Waste*, **44**, 163–168 (1994).
19. A. M. Winer, J. W. Peters, J. P. Smith, and J. N. Pitts Jr., *Environ. Sci. Technol.*, **8**, 1118–1121 (1974).