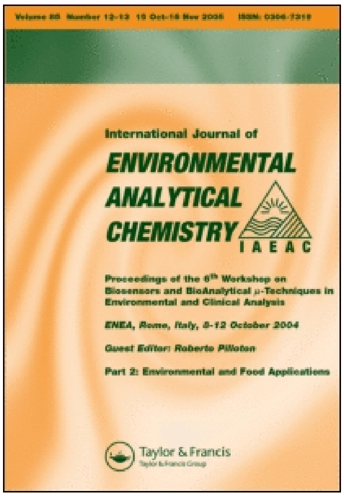

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ATMOSPHERIC DEPOSITION AND CONVERSION OF AMMONIUM TO NITRIC ACID ON A HISTORIC BUILDING: A PILOT STUDY

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Dry and wet deposition on a church tower at Schagen, The Netherlands was estimated by means of sampling with exposure panels. These panels contain several test stones and the runoff water was collected for each stone separately. The runoff samples were analyzed for: Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+}. They were located at a height of 20m on the West and East side of the tower during a pilot study of seven months. The concentrations of gaseous HCl, HNO_3, NH_3, SO_2 and Cl^--, NO_3^--, NH_4^+- and SO_4^{2-}-containing aerosols in air were measured during this field experiment. Precipitation was sampled by means of bulk and wet-only samplers. It is concluded that: (1) Passive sampling by means of exposure panels and analysis of the runoff is a simple method to estimate the total deposition on a monument; (2) acid-deposition-related air pollutants are deposited on the church tower for more than 80% by dry deposition; (3) as a result of the increased turbulence around the church tower, acid dry deposition is increased by at least a factor 10 compared to lower vegetation. The role of ammonium deposition was studied by means of a ^{15}N-enriched ammonium solution added to the surface of stone samples. An increase is observed in the ratio $^{15}N/^{14}N$ in nitrate extracted from the stones. This indicates nitrification of ammonium to nitric acid, which results in increased weathering of a monument by the deposition of ammonium.

KEY WORDS: Dry and wet deposition, acid deposition, monuments, nitrification.

INTRODUCTION

In recent years, air pollution has been recognized to be one of the main causes of the increased weathering of historic monuments in urban and industrialized environments.[1–7] The deposition of air pollutants by dry and wet deposition processes leads to the formation of water soluble salts within the pores and on the surfaces of construction materials. Repeated crystallization and hydration as a function of climatological conditions results in crumbling of the stone. Most laboratory and field studies concerning the effects of air pollution on monuments have been focussed on the formation of gypsum ($CaSO_4.2H_2O$) due to the reaction of deposited sulphur oxide and sulphates with calcium carbonate in construction materials such as limestone, marble and cement mortal. However, the effects of deposited ammonium, nitrate and chloride have hardly been studied.[8–11]

Evaluation of recent publications leads to the conclusion that the dry deposition on monuments of air pollutants, such as gaseous SO_2, HCl, HNO_3 and NH_3, and NH_4^+-, NO_3^--, SO_4^{2-}- and Cl^--containing aerosols has not been determined. Furthermore, no data are available on the effects of components deposited by precipitation. As a consequence it is hardly possible to correlate quantitatively the observed effects with the dry and wet deposition of sulphur-, nitrogen- and chloride-containing pollutants.

The estimation of dry deposition as the product of the dry deposition velocity and air concentration of a component is difficult in the case of buildings. This is a consequence of the complex microclimatological conditions and the variety of construction materials.[12] The measurement of wet deposition by means of wet-only samplers is rather complicated and expensive for extensive use on monuments.

Measurement of the dry and wet deposition on a monument by a passive sampling technique, such as exposure panels was proposed in several papers, with and without the collection of runoff water.[11,13,14] In the most extensive study the atmospheric conditions during field experiments are characterized only by SO_2 air concentration levels and the composition of precipitation.[11]

The first objective of this paper is the evaluation of a standard method for the measurement of dry and wet deposition of chloride-, nitrogen- and sulphur-containing air pollutants on monuments by means of exposure panels and collection of runoff samples. During seven months the deposition under field conditions on a church tower at Schagen (The Netherlands) was measured by analyzing the runoff water of exposure panels.[15] This deposition was related to the air concentrations of gaseous SO_2, HCl, HNO_3 and NH_3, and NH_4^+-, NO_3^--, SO_4^{2-}- and Cl^--containing aerosols measured by a SO_2-monitor and denuder/filter pack techniques,[16–19] and the wet deposition as determined by bulk and wet-only samplers.[20]

The second objective of this paper is a study of the nitrification of ammonium to nitric acid on stone samples. Nitrification of ammonium to nitric acid by microorganisms in forest soils is well known from acid deposition effect studies.[21] The presence of these types of microorganisms on buildings in the Federal Republic of Germany has been reported.[22] This indirectly indicates the formation of damaging nitric acid on monuments after deposition of ammonium. Until now, however, the importance of nitrification on the increased weathering of construction material has not been quantified.[23] Especially in The Netherlands, with its high emissions of NH_3, the damaging effect may be significant.[24]

In the present work, a pilot study was performed by means of ^{15}N isotopic enriched ammonium sulphate added to the surface of weathered stones. The formation of ^{15}N-enriched nitrate on the stones was used as an indication for the nitrification reaction.

EXPERIMENTAL

Field Locations

During the period from September 1987 to April 1988, a field study was

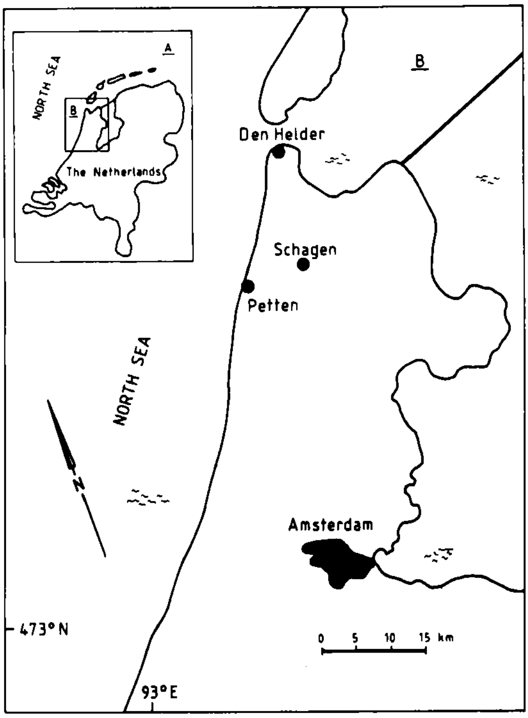

Figure 1 The field locations.

undertaken on a church, built in the nineteenth century, at Schagen, (The Netherlands). Rain and air concentrations of pollutants were measured at existing monitoring stations within a distance of about 10 km. The locations are indicated in Figure 1.

At Den Helder and Schagen precipitation was collected by wet-only and bulk samplers. At Petten air concentrations of the gases SO_2, HCl, HNO_3 and NH_3, and NH_4^+-, NO_3^--, SO_4^{2-}- and Cl^--bearing aerosols were measured at ground level (1.5 m). From a tower-based study up to 150 m on the vertical distribution of air pollutants over grasslands, it is anticipated that these measurements at ground level are a good estimate for air concentrations at an altitude of 20 m height.[25] No significant variability in the air and rain concentrations between these field locations are expected, as large-scale air pollution is studied and no local sources of air pollution are present.

Exposure Panels

At 20 m height on the church tower two exposure panels were attached; one at the West side and the other at the East side. The polyethene panels contain the following test samples: one polyethene sheet, eight carbonate stones and three siloxane-coated carbonate stones (Silox-Seal, Chemprotech, Soest, The

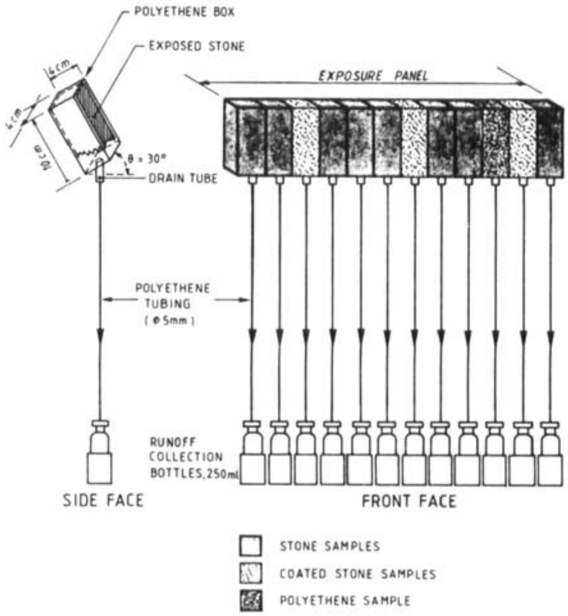

Figure 2 The side and front faces of the exposure panel.

Netherlands). The use of chemical tretment by water repellent reagents has been discussed in several papers.[26,27]

The stones consist for more than 99% of $CaCO_3$ and have a porosity volume of 10–20%. The samples have a length of 10 cm, a width of 4 cm and a height of 4 cm. The collection surfaces of 40 cm^2 are exposed to ambient air at an angle of 60°. In Figure 2 an exposure panel is shown. On top of the exposure panels wires of nylon are attached to ward off birds.

Sampling Strategy

The runoff water of the 24 exposed samples was sampled weekly during the period from September to November 1987 and two-weekly during the period from November 1987 to April 1988. Runoff samples were collected in 250 ml polyethene bottles, which were connected to the exposure panels by means of polyethene tubing, 1 m in length and 0.5 cm in diameter. Microbiological activity in the collection bottles was reduced by the addition of HgI_2. At the start and the end of the field experiment the stones were weighed after 24 h drying at 105 °C and cooling in a desiccator.

Two bulk precipitation samplers with a collection surface of 400 cm^2 were placed on the West and East side at the church tower next to the exposure panels. At ground level a third bulk sampler was located at a distance of about 2 km from the church. The bulk samplers were sampled at the same frequency as the exposure panels. At Den Helder precipitation was collected on a daily basis by four wet-only samplers as a reference for the wet deposition collected by the bulk samplers.

Air concentrations of the gases HCl, HNO_3 and NH_3, and NH_4^+-, NO_3^--, SO_4^{2-}- and Cl^--containing aerosols were measured daily at Petten by means of denuder/filter packs with a sampling time of 24 h. At Petten the air concentrations of SO_2 were monitored as part of the Dutch National Air Monitoring Network (RIVM, Bilthoven, The Netherlands).

Chemical Analysis

The runoff samples were filtered over a 0.45 μm PTFE filter. Precipitation and runoff samples were analyzed by ion chromatography and atomic absorption spectrometry for pH, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}.

After the exposure period of seven months, the depth of weathering of the stone samples was studied by grinding off layers of 1 mm at 1 mm, 5 mm and 10 mm depth. An aliquot of 0.5 g of the obtained material was extracted for 24 h with 50 ml double-demineralized water. The extracts were filtered over a 0.45 μm PTFE filter and analyzed for pH, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+. The formation of $CaSO_4$ in the exposed stones was investigated by scanning electron microscopy (SEM).[28] Slices of the samples were analyzed for the presence of sulphur as a function of depth.

Nitrification Study

In order to investigate the conversion of ammonium to nitric acid on stones, a solution of isotopic ^{15}N-enriched ammonium sulphate was added to the surfaces of fresh and weathered stones. The increase of the $^{15}N/^{14}N$ ratio in nitrate extracted from the surfaces is a measure of the nitrification reaction. This ratio was measured by gas mass-spectrometry using a Finnigan Mat 251.

During November 1987–April 1988, a preliminary experiment was performed using fresh stones, identical to those used in the field experiment, and weathered carbonate stones. During July 1988–November 1988, a second experiment was conducted with four stones, which had been exposed during the previous field experiment. These stones showed green spots, which indicated biological activity on the exposed surfaces.

To the stone samples 20 ml of a 1.5 g 10% ^{15}N-$(NH_4)_2SO_4$ solution per liter was added (Isotec Inc., Miamisburg, Ohio, USA). The natural abundance of ^{15}N is 0.3663% of total nitrogen.[29] The stone samples were placed at Petten in ambient air in a ventilated box, which shielded the samples from precipitation to prevent loss of ^{15}N by runoff water. Once a week the samples were wetted with double-demineralized water to maintain microbiological activity. At the end of the experiments the stones were rinsed with double-demineralized water, the water was filtered over 0.45 μm PTFE filter and the solutions were analyzed for NH_4^+ and NO_3^-. Subsequently, ammonium was removed from the extraction solutions by the following procedure:

—to 80 ml of the solutions 5 ml 1 M NaOH was added,
—the solutions were evaporated to dryness in 12 h at 70 °C,
—the residues were dissolved in double-demineralized water, and evaporated to dryness.

Nitrate in the residues was reduced to ammonium by the procedure of Devarda and oxidized to N_2 by that of Rittenburg.[30, 31] The $^{15}N/^{14}N$ ratio of the obtained N_2 was measured by mass spectrometry. The procedure was validated by solutions of 10% ^{15}N-enriched ammonium and nitrate with a "natural" ^{15}N percentage of 0.3663%. The whole procedure yielded NO_3^- with an average ^{15}N percentage of 0.3639% and a relative standard deviation of 0.5% (N=4), which reflects the efficiency of the separation of nitrate and ^{15}N-enriched ammonium.

RESULTS AND DISCUSSION

Measurement of Total Deposition by Exposure Panels

With the total (water-soluble) deposition on the exposure panels as measured by means of runoff samples, one assumes that dry deposited and stone material is washed off by frequent showers. As shown below by the analysis of the exposed samples after the field experiment, this is the case for nitrate- and chloride-containing species. However, deposited sulphate is partially bound on the stone by the formation of $CaSO_4$. These observations are in accordance with the solubility of $Ca(Cl)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$ and $CaSO_4.2H_2O$, which are 279, 266 and 0.24 gram per 100 ml of water, respectively.[29] Deposited ammonium is partially lost by volatilization and nitrification processes, which will be discussed below. The concentration of calcium in the runoff samples reflects the weathering of calcium carbonate, which in turn is an indication of the amount of deposited acid.

The first part of Table 1 displays the sum of the deposition of H^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+} in $mMol.m^{-2}$, as calculated from the runoff samples obtained from the exposure panels during the field experiment. The amount of precipitation is given in $Kg.m^{-2}$. Results for non-coated stones (West NC. and East NC.), siloxane-coated stones (West C. and East C.), and polyethene plates (West Ref. and East Ref.), exposed at the West and East side of the church tower, are presented. Furthermore, Table 1 gives the results of the wet-only samplers at Den Helder (Wet-only) and the bulk samplers at Schagen on ground level (ground-Bulk), on the West side (West-bulk) and on the East side of the tower (East-Bulk). In the second part of Table 1 the dry deposition of NH_4^+, NO_3^-, SO_4^{2-} and Cl^- is calculated by subtraction of the wet deposition—measured by wet-only samplers—from the total deposition.

The concentrations of sulphate, chloride and calcium have been corrected for the deposition of sea-salt by using the concentration of sodium as an indicator.[32] In seawater the molar ratios are: Cl^-/Na^+ 1.1, SO_4^{2-}/Na^+ 0.06 and Ca^{2+}/Na^+ 0.02.[29] The non-sea-salt concentration of a component, C^*, in runoff and precipitation samples is calculated from:

$$C^* = C_T - R * C_{Na} \qquad (1)$$

Table 1 Total deposition and the dry deposition on the exposure panels at the church tower at Schagen (September 1987–April 1988) measured by means of runoff samples, bulk and wet-only rain samplers[a]

Total Deposition (wet and dry deposition) in mMol.m^{-2}

Sample type	*NH_4^+*	*NO_3^-*	*SO_4^{2-}*	*SO_4^{2-} Cor.*[d]	*Cl^-*	*Cl^- Cor.*[d]	*Weight*[b] *(kg.m^{-2})*	*Na^+*	*K^+*	*Mg^{2+}*	*Ca^{2+}*	*Ca^{2+} Cor.*[d]	*Ion. Bal.*[c]
West NC.	87	376	701	485	4474	503	190	3609	93	354	1234	1156	1.11
East NC.	316	502	1035	755	5126	−6	246	4665	149	516	1136	1034	1.09
West C.	54	95	184	123	1196	82	255	1012	28	116	268	246	1.12
East C.	125	157	280	203	1465	58	222	1280	43	149	314	287	1.09
West Ref.	24	22	45	27	337	14	231	294	8	34	41	35	1.06
East Ref.	68	38	130	66	1251	81	285	1064	29	120	79	55	1.01
West-Bulk	30	14	27	15	214	−6	338	200	7	24	11	7	1.11
East-Bulk	38	12	28	17	179	−11	190	173	10	20	11	7	1.14
Ground-Bulk	23	18	21	13	138	3	464	123	5	15	10	7	1.05
Wet-Only	22	23	21	13	149	8	463	128	3	15	6	3	1.01

Dry deposition (total deposition minus wet deposition measured by wet-only samplers) in mMol.m^{-2}

Sample type	*NH_4^+*	*NO_3^-*	*SO_4^{2-}*	*SO_4^{2-} Cor.*[d]	*Cl^-*	*Cl^- Cor.*[d]
West NC.	65	353	680	472	4324	495
East NC.	294	480	1014	742	4977	−14
West C.	32	72	163	110	1046	74
East C.	103	135	259	190	1316	50
West Ref.	2	−0	24	14	188	5
East Ref.	45	16	109	53	1102	72
West-Bulk	8	−9	6	2	64	−14
East-Bulk	16	−11	7	4	30	−19
Ground-Bulk	1	−4	0	0	−11	−5

[a] For abbreviations, see text.
[b] Total weight of run-off samples.
[c] Ion balance equals the ratio of the sum of cations and anions.
[d] Sea-salt corrected values.

where C_T is the total concentration for C in the samples, R is the ratio of the concentrations of the component and sodium in bulk seawater, respectively, and C_{Na} is the concentration of Na^+ in the samples.

It is observed that for sulphate the sea-salt fraction is about 20–40% of the total deposited sulphate. For chloride and calcium the sea-salt fractions are more than 90% and less than 10%, respectively. For samples with a large sea-salt component the computation by the sea-salt correction can result in a "negative" anthropogenic deposition.[32] "Negative" deposition of chloride is interpreted as zero anthropogenic deposition in the following data interpretation.

The quality of the analysis was determined by means of the ion balance in the runoff and precipitation samples ("Ion Bal."), calculated from the ratio of the sum of equimolar anions and cations, respectively. The results of the analysis presented in Table 1 have an accuracy better than 15%.

In Figure 3 the total deposition in mMol.m^{-2} (7 months)$^{-1}$ on the various exposed surfaces is shown. The figure illustrates that total depositions of ammonium, nitrate, sulphate and chloride on non-coated stones are higher relative to coated stones, polyethylene sheets and bulk samplers. The large differences may be

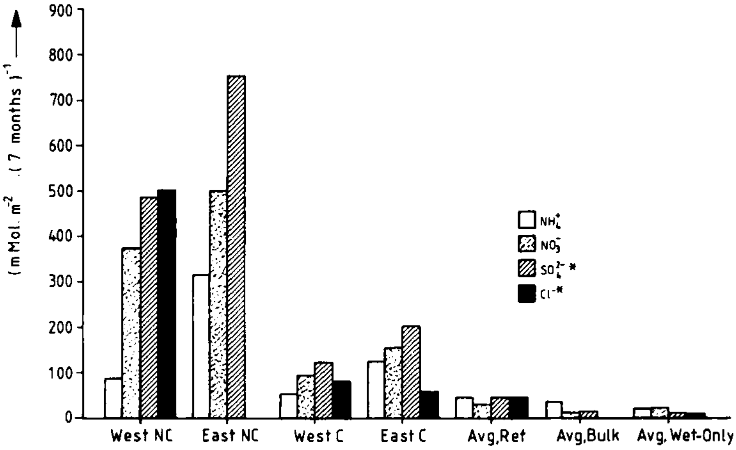

Figure 3 Total deposition of NH_4^+, NO_3^-, SO_4^{2-*} and Cl^{-*} in $mMol.m^{-2}.(7\ months)^{-1}$ on the non-coated stones (West NC. and East NC.), the coated stones (West C. and East C.), the average of the polyethylene plates (Avg. Ref.) and the average of the bulk samplers (Avg. Bulk) at the West and East side of the church tower at Schagen, and the average of the wet-only samplers (Wet-Only) at ground level at Den Helder.

explained by the following mechanism: It is well known from studies on the effects of acid deposition on vegetation that a water layer on a surface drastically increases the dry deposition flux.[33] Due to the porous structure of the non-coated stones it can be expected that a water layer of dew, mist and rain showers is maintained longer on these samples than on the coated stones, the polyethylene sheets and the bulk samplers. Furthermore, the reactivity of the surface of the non-coated carbonate stones towards acid pollutants also enhances the dry deposition on these collection surfaces.

The increased deposition on the East side relative to the West side of ammonium, nitrate, and sulphate reflects the transport of polluted air masses from agricultural areas with high NH_3 emission and industrialized areas on the European continent. The higher deposition of HCl on the West side of the tower suggests the formation of HCl by the reaction of air-borne sea-salt and acid components in polluted air masses transported over the North Sea. From the results in Table 1, it is concluded that polyethylene sheets and bulk rain samplers collect negligible dry deposition compared to the non-coated stones.

It is proposed that polyethene exposure sheets with collection bottles for runoff water are a simple method to measure the wet deposition on a monument. The advantage in comparison with bulk samplers is that they can be placed at various spots on a monument under the same micrometeorological conditions as exposure panels containing construction material of the monument under investigation.

In Figures 4A and 4B the total deposition is given during the field experiment in $mMol.m^2.week^{-1}$ on the non-coated stones at the West and East side of the church tower. The high leaching of Ca^{2+*} during the winter is an indiction of the increased acid deposition as a consequence of increased SO_2 and NO_x emissions.

In Figure 5 the fractions of dry and wet deposition on non-coated and coated

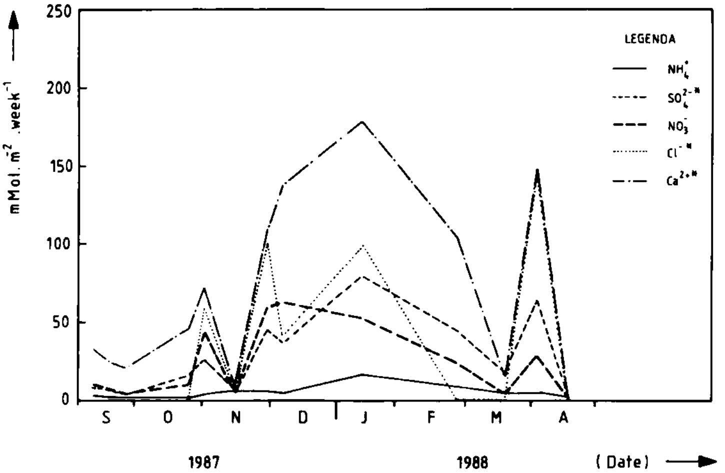

Figure 4A Total deposition of NH_4^+, NO_3^-, SO_4^{2-*}, Cl^{-*}, and the weathering of Ca^{2+*} in $mMol.m^{-2}.week^{-1}$ in relation to the non-coated stones at the West side of the church tower during the field experiment.

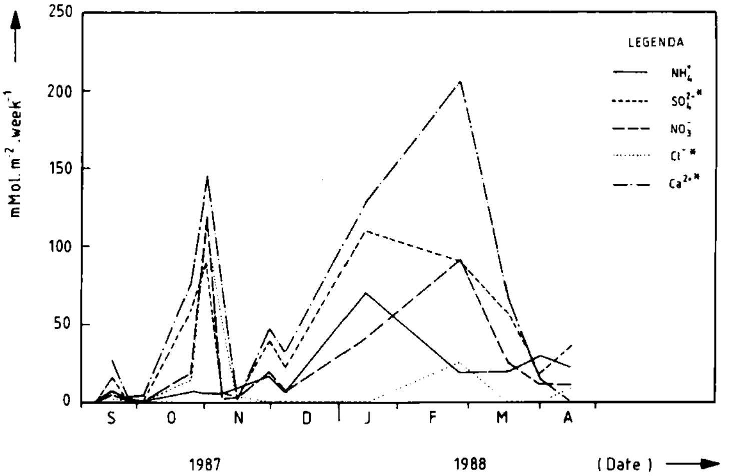

Figure 4B Total deposition of NH_4^+, NO_3^-, SO_4^{2-*}, Cl^{-*}, and the weathering of Ca^{2+*} in $mMol.m^{-2}.week^{-1}$ in relation to the non-coated stones at the East side of the church tower during the field experiment.

stones are given as calculated from the results presented in the first and second part of Table 1. With the exception of ammonium on the West side of the tower, more than 80% of the total deposition is by dry deposition of gases and aerosols. It is concluded that dry deposition is the most important deposition mechanism of acidic pollutants on a building.

The measurement of the dry deposition on a monument using exposure panels was compared with the dry deposition calculated by a micrometeorological method.

The dry deposition flux on a surface is estimated as the product of the air

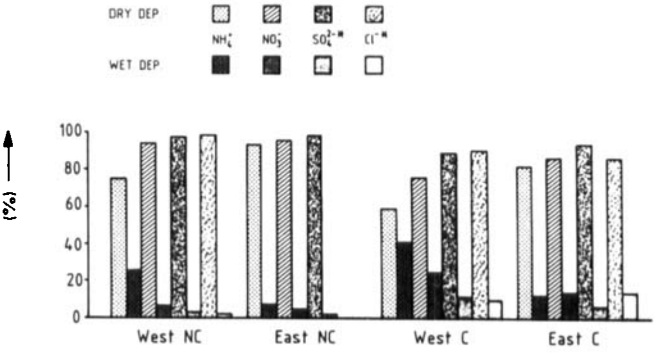

Figure 5 Percentages dry and wet deposition of the total deposition of NH_4^+, NO_3^-, SO_4^{2-*} and Cl^{-*} at the non-coated and coated stones at the West and East side of the church tower, respectively.

Table 2 Dry deposition of NH_3, NH_4^+, HNO_3, NO_3^-, SO_2, SO_4^{2-}, HCl and Cl^- estimated from their concentrations in ambient air (ug.m^{-3}) at Petten (The Netherlands) as a function of the dry deposition velocities.

	NH_3	NH_4^+	HNO_3	NO_3^-	SO_2	SO_4^{2-}	HCl	Cl^-
Air concentrations[a]	3.2	3.2	0.4	3.7	15	4.6	1	3.6
Dep. Vel. (cm.s^{-1})[b]	1.5	0.2	2	0.2	2	0.2	2	0.2
Dry Dep. (mMol.m^{-2})[c]	53	7	2	2	88	2	10	4
Dep. Vel. (cm.s^{-1})[d]	15	2	20	2	20	2	20	2
Dry Dep. (mMol.m^{-2})[e]	531	67	24	22	882	18	103	38

[a] Period average of daily measurements (24 h sampling time).
[b] Dry deposition velocities based on lower limits.
[c] Calculated dry deposition based on lower limits (time of exposure 31 weeks).
[d] Dry deposition velocities based on higher limits.
[e] Calculated dry deposition based on higher limits (time of exposure 31 weeks).

concentration and the dry deposition velocity of gases and aerosols during the time of exposure. In Table 2 the average air concentrations of relevant gases and aerosols during the period from September 1987 to April 1988 are given. The dry deposition velocities used are averaged values from the literature,[34,35] which are generally based on measurements over lower vegetation. Their range from 1.5 to 2 cm.s^{-1} for gases, and 0.2 cm.s^{-1} for submicron aerosols are lower limits. In Table 2 the calculated dry depositions of NH_3, HNO_3, SO_2, HCl, NH_4^+, NO_3^-, SO_4^{2-*} and Cl^{-*} are given in mMol.m^{-2} during the field experiment on the church tower.

In Figure 6 the calculated dry deposition ("Calc. Low") is compared with the dry deposition measured by means of the non-coated stones on the tower. In order to compare the results in Figure 6, the calculated dry depositions of NH_3, HNO_3, SO_2 and HCl are given as NH_4^+, NO_3^-, SO_4^{2-*} and Cl^{-*}, respectively. It is concluded that the measured dry deposition on the exposure panels by means of runoff samples for NH_4^+, NO_3^-, SO_4^{2-*} and Cl^{-*} is higher by factors of 5, 100, 20 and 30, respectively, than was estimated.

An explanation of this may run along the following lines. Due to the increased turbulence around a church tower, hither values of the dry deposition velocities can be expected than those used in the estimation. In Table 2 the dry deposition is

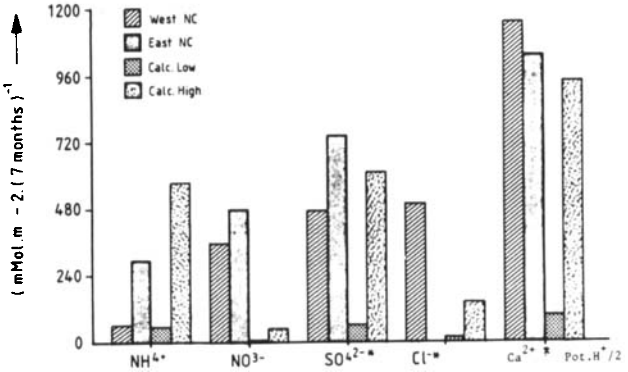

Figure 6 Dry deposition and the amount of leached Ca^{2+*} of non-coated stones ($mMol.m^{-2}.(7\ months)^{-1}$) at the West and East side of the church tower as measured by runoff, and the calculated dry deposition and the potential H^{+*} deposition/2 by means of low and high dry deposition velocities.

estimated also based on dry deposition velocities, which are higher by an order of magnitude. In Figure 6 these values are given as "Calc. High". It follows that increased dry deposition velocities can agreeably explain the discrepancy for SO_4^{2-*} and Cl^{-*}.

However, using these higher values the calculated dry deposition for NH_4^+ and NO_3^- is over- and underestimated, respectively. Reactions on the collection surface can explain these differences. Volatilization and nitrification of deposited ammonium results in loss of ammonium, while the latter process causes an increase of nitrate. Another source of nitrate is the dry deposition of gaseous NO_x, the formation of HNO_2 in the aqueous layer and the oxidation to HNO_3. However, more experimental work is needed in order to quantify these processes.

The leaching of Ca^{2+*} was compared with the calculated potential acid deposition (Pot. H^+). The potential H^+ flux can be calculated from Eq. (2):

$$\text{Pot.}\,H^+ = (2{*}SO_2 + HNO_3 + HCl) \qquad (2)$$

and expressed in $mMol.m^{-2}$ during seven months. The terms SO_2, HNO_3 and HCl refer to the calculated dry deposition of these gases given in Table 2. The potential H^+ deposition during the field period is calculated by Eq. (2) as 188 and 1880 mMol $H^+.m^{-2}$ for the lower and higher dry deposition velocities, respectively. The calculated amount of Ca^{2+*} leached from the stones by this amount of acid deposition, equals Pot. $H^+/2$, that is 94 and 940 $mMol.m^{-2}$. The averaged measured Ca^{2+*} in the runoff samples is 1100 $mMol.m^{-2}$ of the non-coated stones, which is in better agreement with the higher dry deposition velocities. In Figure 6 these values are given. The figure illustrates the hypothesis that the dry deposition of gases (and aerosols) on a monument is increased at least by a factor of 10 compared to dry deposition on lower vegetation.

Analysis of the Stone Samples after the Field Experiment

After the field experiment the non-coated stones were examined by chemical analysis and scanning electron microscopy. Difference in the weights of the

Table 3 NH_4^+, NO_3^-, SO_4^{2-} and Cl^- in extracts of stone samples as a function of depth.

Type	*Depth (mm)*	*NH_4^+ (mg.l^{-1})*	*NO_3^- (mg.l^{-1})*	*SO_4^{2-} (mg.l^{-1})*	*Cl^- (mg.l^{-1})*
West NC.[a]	0	0.2	1.2	4.4	1.7
	10	0.2	0.7	2.8	1.2
	20	0.1	0.5	2.9	1.0
East NC.[a]	0	0.1	0.8	3.8	0.8
	10	0.1	0.4	2.2	0.7
	20	0.1	0.4	2.4	0.7
West C.[a]	0	0.1	0.6	2.4	0.7
	10	0.1	0.5	2.0	0.8
	20	0.1	0.6	1.8	0.7
East C.[a]	0	0.1	0.6	2.1	1.3
	10	0.1	0.4	1.7	0.5
	20	0.1	0.5	1.8	0.6

[a]Average of three stone samples; non-coated and coated carbonate stones exposed at the West and East side of the tower.

samples before and after the field experiment were negligible. The overall mass loss was in the order of 0.2%, which is about 0.5 g on an average weight of 300 g of the stone samples. Loss of calcium carbonate is obviously compensated by the formation of $CaSO_4$. To investigate the depth of weathering, samples of the stones were taken from the surface, and at 10 mm and 20 mm depth, subsequently extracted by means of demineralized water and the extracts analyzed for NH_4^+, NO_3^-, SO_4^{2-} and Cl^-. The results are given in Table 3. For the non-coated stones decreasing concentration gradient with depth is observed for SO_4^{2-}. This gradient is less pronounced for NO_3^- and Cl^-. This suggests that gypsum is not only formed on the surface of the stones, but also within the pores and that next to $CaSO_4$, also nitrate- and chloride-containing salts are present within those pores. Only traces of ammonium could be detected within the samples.

Slices of the exposed stones were examined by means of scanning electron microscopy to study the formation of gypsum, but no detectable amount could be measured above the detection limit of 0.1% S.

Nitrification of Ammonium on a Monument

In Table 4 the results are given of a tracer experiment with 10% ^{15}N-enriched ammonium sulphate added to stone surfaces in July 1988. The stones were exposed at ambient conditions until November 1988. An increase of the natural 0.3663% ^{15}N of nitrate after the exposure time will indicate nitrification of ammonium to nitrate on the surface.

Four non-coated stones were used, which had been exposed on the West and East side of the tower at Schagen during the field experiment. The amount of ammonium and ^{15}N added are given in Table 4. The background amount of ^{15}N present is negligible in comparison to the added 50 μMol ^{15}N. After four months of exposure to ambient air, but shielded from precipitation to prevent loss of ^{15}N by runoff, the stones were extracted with water.

Table 4 Results of a tracer experiment with 10% ^{15}N-enriched $(NH_4)_2SO_4$ solution (1.5 g.l^{-1}) brought on the surface of the stones, and exposed to ambient air at Petten (The Netherlands) from July to November 1988.

Date 12 July 1988	*Added NH_4^+ (mg)*	*Added ^{15}N (μMol)*
West NC.[a]	9.01	50
West NC.[a]	8.50	47
East NC.[a]	8.55	47
East NC.[a]	8.76	49

Date 17 November 1988	*Recovery[b] NH_4^+ (mg)*	*(%)NH_4^+ Recov./Added*	*Recovery[b] ^{15}N (μMol)*	*(%) ^{15}N Recov./Added*
West NC.[a]	0.10	0.19	0.20	1.1
West NC.[a]	0.09	0.19	0.82	1.0
East NC.[a]	0.10	0.22	0.48	1.2
East NC.[a]	0.15	0.31	0.27	1.7

Date 17 November 1988	*Recovery[b] NO_3^- (mg)*	*Recovery[c] ^{15}N (%)*
West NC.[a]	2.72	0.8185
West NC.[a]	2.17	2.6964
East NC.[a]	5.23	0.9380
East NC.[a]	1.41	1.5615

[a] Non-coated stones exposed during the field experiment.

[b] Calculated from the results of the analysis of extraction solutions.

[c] Percentage ^{15}N of nitrate in the extraction solution; natural percentage is 0.3663%.

The observed concentrations of NH_4^+ and NO_3^- in the extraction solutions are shown in Table 4. Comparison of added ammonium and recovered ammonium indicates that more than 98% of the added ammonium is lost. The percentages ^{15}N of the nitrate in the extraction solution of the four stones are 0.8185, 2.6964, 0.9380 and 1.5615%, respectively, which is a significant increase compared to the natural percentage of 0.3663%. It indicates nitrification by microorganisms. This also follows from an identical experiment from November 1987 to April 1988 with fresh and weathered carbonate stones without traces of microorganisms. No increase in the $^{15}N/^{14}N$ ratio of nitrate was observed as a consequence of the absence of microorganisms and the winter season.

Though the ^{15}N experiment is a qualitative proof of nitrification of ammonium to nitric acid on stone samples, its quantitative value is uncertain. The results given in Table 4 show that less than 1% of the added ^{15}N is recovered in the extraction solutions. This suggests that the ^{15}N is lost from the stones either before or after nitrification.

Results from laboratory experiments indicate that less than 1% of ammonium is recovered from a $(NH_4)_2SO_4$ solution added on a fresh carbonate stone, which as been dried during 24 h at ambient temperature. This indicates that ammonia, which is deposited in a moisture film, is lost by volatilization during drying. The amount of ammonium transformed by nitrification during the moisture period is not known.

The question arises whether ammonia was deposited in the alkaline aqueous layer on carbonate stones. The measured pH's of the extraction solutions of the stone samples, which were exposed during the field experiment at Schagen, indicate that the pH of the water layer was from 6.5 to 7.8. The ratio's NH_4^+/NH_3 of the reaction:

$$NH_3 + H_2O <\text{----}> NH_4^+ + OH^- \tag{3}$$

at pH 7, pH 8 and pH 9 are 175, 17.5 and 1.75, respectively.[29] Consequently, it is expected that NH_3 easily dissolves in an aqueous solution with a pH of up to 8. This was confirmed by laboratory experiments with test gas mixtures of NH_3 flowing over an aqueous layer of $pH < 8$, in which ammonia was dissolved readily.

It is concluded that ammonia is deposited on monuments, and that the rate of nitrification reaction during the moisture period determines the damaging effect.

CONCLUSIONS

From a field study of 7 months on a church tower at Schagen (The Netherlands) it is concluded that total deposition on a monument can be measured by means of a simple passive sampling technique, such as exposure panels and collection of runoff samples. The wet deposition is determined by polyethene test plates.

Advantages of this technique are the use of collection surfaces of the same material as the monument under research and the simple setup and small dimensions of the collection device which can be applied at various spots on the building. Furthermore, protective measures (e.g. coatings on stones, various stone types for restoration) can be tested by means of exposure panels.

From this study it is concluded that dry deposition by gases (e.g. NH_3, HNO_3, SO_2 and HCl) and aerosols (e.g. NH_4NO_3 and $(NH_4)_2SO_4$) accounts for more than 80% of the total anthropogenic deposition. Acid dry deposition is predominantly determined by the deposition of gases, such as SO_2, HNO_3 and HCl, which is reflected in leaching of calcium from the carbonate stones. Comparison with the average acid deposition on lower vegetation leads to the conclusion that the acid deposition on a monument is drastically increased by at least a factor of 10, which must mainly be attributed to increased dry deposition.

Examination of the runoff samples and slices of the exposed samples revealed that deposited chloride and nitrate predominantly form soluble salts, and that effects are mostly related to the deposition of H^+. Deposited sulphate forms the less soluble gypsum, which is the main damage mechanism of carbonate stones. The main role of precipitation is cleaning the monument from dry deposited material, but after a shower the wet surfaces will undergo increased dry deposition processes.

The role of ammonium deposition is uncertain. From the results of laboratory experiments and the field study it is concluded that deposited ammonium is volatilized upon drying of the surface. However, the large excess of the measured dry deposited nitrate compared to the calculated value suggests formation of nitrate by nitrification on the monument. It was confirmed by a ^{15}N tracer study that ammonium is nitrificated to nitric acid by microorganisms, thereby increasing the weathering of the monument.

Future work will deal with the measurement of the dry and wet deposition on monuments at urban, rural and coastal areas by means of exposure panels with various construction materials and in combination with ambient air measurements by denuder/filter pack techniques. The measurement of the presence of moisture on the exposure panels (e.g. dew, mist and precipitation) and the correlation of this parameter with the dry deposition flux is an important next objective.

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