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Biodeterioration of natural stone with special reference to nitrifying bacteria

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Abstract

An evaluation of field data from historical buildings in Germany showed that chemoorganotrophic bacteria are the most numerous microorganisms in building stones, followed by fungi and nitrifying bacteria. Chemoorganotrophic bacteria and fungi were present in almost every sample. Ammonia and nitrite oxidizers were found in 55 and 62% of the samples, respectively. Within months, natural stone was colonized by chemoorganotrophic microorganisms. The highest cell numbers were usually found near the surface. The colonization of natural stone by nitrifying bacteria took several years. The highest cell numbers were in some cases found underneath the surface. Nitrifying bacteria showed a preference for calcareous material with a medium pore radius between 1 and 10 μm. Cell numbers of nitrifying bacteria did not correlate to the nitrate content of the stone material. We demonstrated that the stone inhabiting microflora can cause significant loss of nitrate by denitrification. Our data strongly suggested that microbial colonization of historical buildings was enhanced by anthropogenic air pollution. Samples taken from stone material with a pore radius ≤ 1 μm had significantly higher cell numbers when they were covered with black crusts. A comparison of samples taken between 1990–1995 from buildings throughout Germany showed that in Eastern Germany a significantly stronger colonization with facultatively methylotrophic bacteria and nitrifying bacteria existed. The same was true for natural stone from an urban exposure site when compared to material from a rural exposure site. Data from outdoor exposure and laboratory simulation experiments indicated that the colonization of calcareous stone by nitrifying bacteria was enhanced by chemical weathering.

Abbreviations: CFU – colony forming units; FDE – field data evaluation; IG – Ihrlersteiner green sandstone; LSE – laboratory simulation experiments; MPN – most probable number; *n* - number of samples; OEE – outdoor exposure experiments; PPFM – pink-pigmented facultatively methylotrophic bacteria; SS – Sander sandstone

Introduction

Weathering of natural stone exposed to the atmosphere is caused by a combination of physical, chemical, and biological processes. The decay of historical buildings results in high expenses for repair and preservation (Vieser 1987; Gauri 1990; Flemming 1996). In the absence of industrial influence, carbon dioxide is the main cause for chemical weathering of calcareous stone (Gauri 1990; Gauri et al. 1992). Since the beginning of the 20th century, the rate of stone decay has increased as a result of industrial air pollution (Luckat 1973; Grimm 1987; Rosvall 1988; Leysen et al. 1989). Sulphur dioxide has long been known as one of the main factors of chemical weathering (Spedding 1969; Braun & Wilson 1970; Luckat 1973; Gauri & Holdren 1981; Johansson 1990; McGee et al. 1992; Nord et al. 1994). The reaction of sulphur dioxide with building stone results in a sulphuric acid attack, with concomitant enrichment of the material with gypsum, and strongly contributes to the formation of black crusts (Camuffo et al. 1982, 1983). Although sulphur

dioxide emissions in Western Europe have been decreasing since the 1970s (Biedenkopf 1985; Eggleston et al. 1992; Anonymous 1992), outdoor exposure experiments clearly demonstrated that sulphur dioxide is still the main agent of chemical weathering (Lipfert 1989; Seevers & Van Grieken 1992; Webb et al. 1992; Steiger et al. 1993). Recently, the role of nitrogen oxides and their reaction products in chemical weathering of building stones has attracted considerable interest (Delopoulou & Sikiotis 1992; Haneef et al. 1992; Kirkithsos & Sikiotis 1996; Behlen et al. 1996, 1997).

Several investigations during the last 10–15 years have made it apparent that, in addition to chemical weathering, microbiologically induced weathering contributes to the deterioration of building stone (Lyalikova & Petruschkova 1991; Ortega Calvo et al. 1991; Palmer et al. 1991; Griffin et al. 1991; De la Torre et al. 1993a; May et al. 1993; Bock & Sand 1993; Warscheid & Krumbein 1996). While atmospheric pollution with sulphur dioxide decreased, the emissions of ammonia, nitrogen oxides, and hydrocarbons have increased or remained on a high level. Ammonia mainly originates from agricultural sources (Buijsmann et al. 1987; Asman et al. 1992), while nitrogen oxides and hydrocarbons can mainly be attributed to traffic and industrial sources (Biedenkopf 1985; Eggleston et al. 1992; Anonymous 1992). Building stone enriched with ammonium, hydrocarbons, and reaction products of nitrogen oxides (Schröder 1991; Saiz-Jimenez 1993; Bock & Fahrig 1993; Nord et al. 1994; Behlen et al. 1996) may support the growth of microorganisms that can use these compounds as substrates. Hydrocarbon-utilizing bacteria (Warscheid et al. 1991) and ammonia and nitrite oxidizers (Bock & Sand 1993) have been isolated from buildings. Endolithic nitrite oxidizers, in addition to nitrite and organic substances, may use nitric oxide as substrate (Freitag & Bock 1990; Mansch 1994; Vollmer 1997). Due to insufficient amounts of reduced sulphur compounds in the atmosphere (Garland 1978), thiobacilli were rarely detected on historical buildings (Bock & Sand 1993). The same was true for bacteria oxidizing carbon-monoxide (Prignitz 1995). Although the atmospheric concentration of methane has increased (Lacis et al. 1981; Badr et al. 1991), it seems that methane-oxidizing bacteria cannot grow in building stones with the current methane level, unless in the presence of methanogenic bacteria (Wilimzig et al. 1995; Kußmaul et al. 1998).

One of the main difficulties in understanding and evaluating the role microorganisms play in stone deterioration is the fact that physical, chemical, and microbiological weathering simultaneously act together and interact with each other. These difficulties prompted us to apply three different approaches in studying the role of endolithic microorganisms, especially nitrifying bacteria, in deterioration of natural stone. From 1985 up till 1995 field data evaluation (FDE), outdoor exposure experiments (OEE), and laboratory simulation experiments (LSE) were performed. Field data suffer most from the complexity of natural conditions. Therefore, they can only be representative when a high quantity of samples is investigated. Furthermore, the presence of certain microorganisms alone does not confirm their role in biodeterioration. OEE are time-consuming (years to decades), but have the advantage that exposure-time and stone characteristics are known and climatic and environmental factors are available. In LSE, the weathering potential of microorganisms isolated from building stones can be demonstrated and quantified within a relatively short time (several months to a year). In addition, simulation experiments are a unique tool for testing different materials, protecting agents, and other countermeasures under controlled conditions.

This paper focusses on fungi, chemoorganoheterotrophic bacteria, and chemolithoautotrophic nitrifying bacteria. Although algae and cyanobacteria were not investigated, a short description of their role in biodeterioration is presented. In spite of the fact that the different groups of microorganisms are discussed separately, it should be kept in mind that microbial growth on natural stone is bound to biofilms comprised of mixed populations. Furthermore, the characteristics of cells in biofilms are different from single cells (Flemming 1991; Costerton et al. 1987, 1995). The reader can refer to the literature for the role of higher plants (Mishra et al. 1995; Schober et al. 1995) and lichens (Gehrmann et al. 1988; Jones et al. 1988; Ariño et al. 1995) in biodeterioration. Biogenic damage mechanisms have been reviewed by Berthelin (1983), Sand (1996), and Warscheid & Krumbein (1996). The possible role of microbial melanins in discoloration of building stones was summarized by Saiz-Jimenez (1995).

Microorganisms involved in biodeterioration

Algae and phototrophic bacteria

Photoautotrophic algae and cyanobacteria grow independently from the supply of organic substrates and, therefore, belong to the primary colonizers of building stones (Strzelczyk 1981). While algae are primarily found in relatively moist areas (Lyalikova & Petushkova 1991; Ortega-Calvo et al. 1995), cyanobacteria are also present in dry parts of buildings (Saiz-Jimenez et al. 1990; Ortega-Calvo et al. 1991). The enrichment of organic substances on stone material due to growth of phototrophic organisms may support the development of chemoorganotrophic microorganisms (Lyalikova & Petushkova 1991; De la Torre et al. 1991; Palmer & Hirsch 1991). Although there is no direct evidence for a role of phototrophic microorganisms in chemical weathering, biofilms of algae and cyanobacteria may impose mechanical stress on the material (Ortega-Calvo et al. 1991), change the water characteristics of the material (Warscheid et al. 1993; Ortaga-Calvo et al. 1995), and contribute to discoloration (Warscheid & Krumbein 1996).

Chemoorganotrophic bacteria

Natural stone exposed to the atmosphere is colonized with numerous chemoorganotrophic bacteria within months (Braams 1992). Many chemoorganotrophic bacteria can live under oligotrophic conditions and, therefore, belong to the primary colonizers of building stones (Wainwright et al. 1993; Warscheid & Krumbein 1996). Although some chemoorganotrophs can grow under oligotrophic conditions, an enrichment of hydrocarbons on building stone may support the growth of chemoorganotrophic bacteria (Warscheid et al. 1991; Saiz-Jimenez 1993). It is difficult to estimate the weathering potential of this group, as diverse genera with different metabolic activities belong to the stone inhabiting chemoorganotrophic microflora. Acidogenic and non-acidogenic representatives were isolated (Palmer et al. 1991; Krumbein et al. 1992). As high numbers of airborne chemoorganotrophic bacteria are deposited on buildings (Eckhardt 1996), it is impossible to distinguish between actively growing or adsorbed bacteria (Bock & Sand 1993). Nevertheless, adverse effects on building stones through strong colonization by chemoorganotrophic bacteria are likely to be caused by carbon dioxide production, biofilm formation, and discoloration (Warscheid & Krumbein 1996).

Fungi

The colonization of natural stone by fungi depends on the colonization by chemoorganotrophic bacteria; hence, fungi seem to be secondary colonizers of building stones (Braams 1992; Bock & Fahrig 1993). Acidogenic as well as non-acidogenic fungi were isolated (Palmer et al. 1991; De la Torre et al. 1991; Gómez-Alarcón et al. 1995). The strong potential of acidogenic fungi to attack mineral materials has been shown by several authors (Henderson & Duff 1963; Eckhardt 1979; De la Torre et al. 1993a). De la Torre et al. (1993b) demonstrated that fungi can be involved in crust formation on different stones. Some genera of fungi are involved in discoloration through the formation of melanins (Warscheid & Krumbein 1996; Saiz-Jimenez et al. 1995). Fungi isolated from building stones produced a similar spectrum of organic acids, as found in samples from buildings (Palmer et al. 1991; Bock & Sand 1993). According to Palmer et al. (1991), *in situ* cation chelation by microbially produced organic acids may be the main effect of fungal weathering. Furthermore, results of De la Torre & Gómez-Alarcón (1994) indicate that filamentous fungi are involved in biogenic iron and manganese oxidation in natural stone.

Chemolithotrophic bacteria

Chemolithoautotrophic bacteria can derive their energy from the oxidation of reduced inorganic substances. They are able to use carbon dioxide as their main carbon source. Endolithic nitrifying bacteria are the main representatives of the chemolithoautotrophic microflora in building stones (Bock & Sand 1993). The two-step microbial conversion of ammonium to nitrate catalyzed by nitrifying bacteria is called nitrification. Ammonia oxidizers oxidize ammonium to nitrous acid, which is used by nitrite oxidizers as a substrate and is oxidized to nitrate:

$NH_4^+ + 1\,{}^1/_2\,O_2$	$\rightarrow$	$NO_2^- + H_2O + 2H^+$	ammonia oxidizers
$NO_2^- + 1/2\,O_2$	$\rightarrow$	NO_3^-	nitrite oxidizers
$NH_4^+ + 2\,O_2$	$\rightarrow$	$NO_3^- + H_2O + 2\,H^+$	nitrification

The significance of nitrifying bacteria for biodeterioration was first indicated by Kauffmann (1953), Wagner & Schwartz (1965), and Krumbein (1968). The activity of nitrifying bacteria in natural stone causes a biogenic nitric acid attack and an enrichment with nitrates (Bock 1987; Sand et al. 1989;

Bock & Sand 1990; Bock et al. 1991; Bock & Sand 1993). The weathering potential of nitrifiers has been demonstrated in LSE (Bock et al. 1989; Mansch & Bock 1994, 1996). Investigations of Baumgärtner et al. (1989, 1991) demonstrated that endolithic nitrifying bacteria contribute to nitric oxide emissions from building surfaces.

During the last ten years, the nitrifying microflora of historical buildings in Germany was quantified and characterized. Endolithic ammonia oxidizers isolated from building stone belong to the genera *Nitrosomonas*, *Nitrosovibrio*, and *Nitrosospira* (Meincke et al. 1988; Spieck et al. 1992), which are all members of the β-subdivision of the Proteobacteria (Koops & Möller 1992; Teske et al. 1994). According to Meincke et al. (1989), *Nitrosovibrio* species are dominant. On the basis of automated pattern matching of proteins, all nitrite oxidizers isolated from buildings were assigned to the genus *Nitrobacter*. The majority of strains belonged to the species *Nitrobacter vulgaris* (Bock et al. 1990; Krause-Kupsch 1993; Spieck et al. 1995). Recent investigations of freshwater environments using phylogenetic oligonucleotide probes (Mobarry et al. 1996) indicate that *Nitrobacter*, although frequently isolated, may not be the dominant genus in aquatic environments (Wagner et al. 1996; Hovanec et al. 1998). Therefore, members of other genera among the phylogenetically diverse nitrite oxidizing bacteria (Bock & Koops 1992; Teske et al. 1994; Hovanec et al. 1998) may also be present in building stone.

Chemolithoautotrophic thiobacilli grow on reduced sulphur compounds. Similar to nitrifying bacteria, they have a strong weathering potential (Sand & Bock 1991). However, thiobacilli were seldom found on historical buildings in Germany (Bock & Sand 1993).

Material and methods

Historical buildings

Between 1985 and 1995, more than 1500 samples from 44 buildings in Germany and 3 buildings located in other European countries were taken and analysed for microbiologically parameters. Based on these data we evaluated the endangerment of historical buildings by microorganisms (Bock et al. 1991; Bock & Fahrig 1993; Bock et al. 1998). For the analysis given here, only samples from natural stone were considered. Material with a calcareous (dolomitic), siliceous, clayish, and siliceous-clayish-ferric binding material was distinguished.

The comparison of data from Eastern Germany (n = 314), meaning the former German Democratic Republic, with data from Western Germany (n = 753) includes samples of mortar and natural stone.

Statistical analysis of data of a few buildings (Wilimzig et al. 1992; Bock & Sand 1993; Bock & Fahrig 1993) and for mortar, bricks, and concrete (Bock et al. 1994; Wilimzig & Bock 1996; Wilimzig 1996; Jozsa et al. 1996a, b; Bock et al. 1998) were published earlier.

Outdoor exposure sites

Specially cut specimens (roughly 80 $\times$ 20 $\times$ 30 cm) from natural stones have been exposed since 1986/87 on exposure sites in Duisburg (urban) and Holzkirchen (rural) (Brüggerhoff & Wagener-Lohse 1989). Data on the initial microbial colonization of the materials were reported by Braams (1992) and Warscheid et al. (1993).

The Duisburg site is characterized by a more moderate climate and a significantly higher level of industrial air pollution, especially sulphur dioxide and dust (Steiger et al. 1993), than the Holzkirchen site. In Holzkirchen, a relatively high level of annual rainfall and a rather extreme climate with quick and frequent temperature changes is typical.

Since 1986, selected specimens in Duisburg have been annually investigated by taking surface samples from a depth of 0–5 mm (Mansch 1994). In 1995, one specimen of Ihrlersteiner green sandstone (IG) and one of Sander sandstone (SS) from each exposure site was thoroughly investigated by chemists, physicists, mineralogists, and microbiologists. Drill-core samples of 22 mm in diameter and about 5 cm length were taken from each site.

In Duisburg after 8 and 9 years of exposure, specimens from SS and IG were enriched with gypsum and showed obvious signs of weathering, e.g. sanding, crust formation, and discoloration (internal reports). In Holzkirchen after 8 years of exposure, specimens of SS appeared relatively sound, while the ones of IG exhibited signs of physical weathering, such as cracks. Those parts of the specimen that had been directly wetted by rain were covered with green to black biofilms composed of algae and other microorganisms.

Laboratory simulation experiments

We have performed laboratory simulation experiments (LSE) since 1987 under controlled conditions to demonstrate the weathering potential of nitrifying bacteria (Bock et al. 1989; Mansch & Bock 1996). Mansch (1994) simulated for the first time a combined chemical and microbiological attack on natural stone by nitrifying bacteria and gaseous pollutants. Two series of sealed specimen ($30 \times 5 \times 5$ cm) from Ihrlersteiner green sandstone were inoculated with nitrifying bacteria and incubated under optimal conditions (high stone moisture, supply of ammonium chloride, 28 °C, 95% r.H.) in controlled climatic chambers. After 9 weeks in ambient air, one series of inoculated test blocks was exposed to a simulated smog atmosphere of 1065 μg/m^3 SO_2, 850 μg/m^3 NO, and about 450 μg/m^3 NO_2 (Figure 7), while the second series was kept in ambient air. A third series of specimen that had not been inoculated was also exposed to the gas atmosphere to demonstrate the influence of chemical weathering in the absence of nitrifying bacteria. In regular intervals, one of the specimen from each series was removed from the chambers and characterized chemically and microbiologically as described by Mansch & Bock (1996). MPN cell numbers were determined as described below.

Stone material

The following characteristics of Ihrlersteiner green sandstone (IG) and Sander sandstone (SS) were taken from Grimm (1990) and internal data from project partners:

Ihrlersteiner green sandstone
Quartz = 36%; calcite/dolomite = 43%; glauconite = 13%; fragments = 0.5%; fossils = 6%; clay-minerals < 2%. binding = calcitic/dolomitic; pH (fresh material) = 8.5; maximum water-holding-capacity = 5.6%; porosity (Vol. %) = 14–18%; pores > 1 μm $\varnothing$ = 80%; pores < 1 μm $\varnothing$ = 20%; maximum in pore size at 20–10 μm; specific surface = 7.2 m^2/g.

Sander sandstone
Quartz = 54%; fragments = 32%; plagioclase = 7%; feldspar = 3%; muscovite = 2%; accompanying minerals = 2%. binding = clayish-cloritic; pH (fresh material) = 7.3; maximum water-holding-capacity = 6.5%; porosity (Vol. %) = 20%; pores > 1 μm $\varnothing$ = 53%; pores < 1 μm $\varnothing$ = 47%; maximum in pore size at 10–2 μm; specific surface = 4.5–7.3 m^2/g.

Sampling

On buildings, surface samples of material originating from a depth of 0–5 mm were taken by hammer and chisel. Drill cores were taken from the specimen at the exposure sites with a tube-like diamond drill, 22 mm in diameter and cooled with compressed air. Each core was cut into slices of 5–15 mm thickness to determine the profile of chemical and microbiological parameters. Likewise, specimens from LSE were cut by hammer and chisel into slices between 5–20 mm and ground by pestle and mortar.

Microflora characterization

Chemoorganotrophic bacteria were counted on DEV-gelatin agar (Merck No. 1.10685), and fungi were quantified on SABOURAUD-maltose agar (Merck No. 1.05439). All cell counts from historical buildings were done with the concentrated media, while data from OEE and LSE were determined with tenfold diluted media. Facultatively methylotrophic bacteria, representing various genera of chemoorganotrophs with the ability to grow on C_1-compounds, were counted on high purity agar (DIFCO, No. 0142-17-0) with methanol as the only substrate. During investigations at the exposure sites, pink-pigmented and non-pigmented colonies were counted separately. The methylotrophs growing as red colonies can be attributed to the group of pink-pigmented facultatively methylotrophic bacteria (Green 1992), while the non-pigmented colonies represent diverse genera of facultatively methylotrophic bacteria (Lidstrom 1992).

Nitrifying bacteria were quantified by a 3-tube MPN test. Potential nitrification activities were measured with suspended material in a basal salt solution containing optimum substrate concentrations. For further details refer to Mansch & Bock (1996).

Chemical methods

Nitrite/nitrate and ammonium were eluted for 12 h (1 g/10 ml) with deionized water or 1 M KCl-solution, respectively. The stone material was sedimented and the supernatant measured by high-performance liquid chromatography (Kontron-Instruments). Separation was performed with an Hypersil ODS 5 μ column. For nitrite and nitrate, a tetrabutylammoniumsulphate/10% methanol buffer with pH 6.5 served as eluent. Both species were detected at 225 nm. To measure the ammonium concentration,

Table 1. Average values of chemical and microbiological parameters for samples of natural stone from historical buildings in Germany. Sampling was done between 1985 and 1995. Cell numbers are given as geometric mean, all other parameters as arithmetic mean. MPN = Most Probable Number, CFU = Colony Forming Units

Parameters	Average	Number of samples	Minimum	Maximum
Ammonium (μg/g)	201	949	0	4441
Nitrite (μg/g)	2.0	930	0	179
Nitrate (μg/g)	1397	1029	0	26660
Sulphate (μg/g)	36445	109	41	434100
pH	6.6	1019	3.7	12.1
Protein (μg/g)	34.4	296	0	921
Ammonia oxidizers (MPN/g)	5.5×10^0	1023	0	5.0×10^4
Nitrite oxidizers (MPN/g)	9.1×10^0	1029	0	8.0×10^5
Chemoorganotrophic bacteria (CFU/g)	3.9×10^4	837	0	5.7×10^7
Fungi (CFU/g)	2.9×10^3	838	0	6.1×10^7
Methylotrophic bacteria (CFU/g)	6.9×10^2	295	0	5.0×10^7
Potential activity of ammonia oxidizers (nmol/h/g)	2.4	485	0	50
Potential activity of nitrite oxidizers (nmol/h/g)	2.7	484	0	50

samples were derivated with o-phthaldialdehyd mercaptoethanol reagent at pH 7 (Corbin 1984), incubated for one hour in the dark, and measured by fluorescence detection ($\lambda_{excitation}/\lambda_{emission}$ 420/470 nm). Acetonitrile/phosphate buffer with pH 7.3 served as eluent. This method captures ammonium and ammonia. The pH of stone material was determined in 1 M KCl (1 g/10 ml).

The sulphate content of stone material was determined at the Institute of Inorganic and Applied Chemistry, University of Hamburg. The samples were one to several times eluted with deionized water and after filtration (0.2 μm) measured by ion-chromatography (DIONEX 2000i). An AS9-SC column and 0.75 mM sodium hydrogencarbonate/2 mM sodium carbonate as eluent were used for separation. Suppression was achieved with an AFS-1 column and 0.025 N sulfuric acid.

Denitrifying activity

To check the stone for denitrifying activity, 0.1–0.5 g of material in 150-ml serum bottles were adjusted with a nitrate solution to approximately 20% of weight stone moisture, flushed with N_2, and incubated for three weeks. The final nitrate content was roughly 200 μg/g nitrate. Organic substrate was not added. The denitrifying potential was expressed as percent of nitrate removed, in comparison to a sterilized control. Samples with > 60% nitrate-loss were classified as positive.

Statistical methods

Because the data from historical buildings were non-normally distributed, correlation analyses were made by the Spearman rank correlation analysis. Two groups of data were compared with the Mann-Whitney U-test (Precht 1982). Cell numbers are expressed as geometric means, while all other parameters are given as arithmetic means.

Results

Field data evaluation (FDE)

Table 1 summarizes the average values of chemical and microbiological parameters measured for natural building stone of historical buildings in Germany. With a geometric mean of 4×10^4 CFU/g, chemoorganotrophic bacteria were the most numerous microorganisms in natural stone from historical buildings. The mean geometric cell numbers of fungi were about ten times and the numbers of facultatively methylotrophic bacteria a hundred times lower than the numbers of chemoorganotrophic bacteria. Mean

Table 2. Colonisation of natural stone samples from historical buildings by fungi and bacteria. Mean geometric cell numbers are calculated for those samples for which the listed microorganisms were detected

Microorganisms	Proportion of samples colonised (%)	Average cell numbers (units/g)	Number of samples
Chemoorganotrophic bacteria	99	4.4×10^4	828
Fungi	95	4.6×10^3	796
Facultatively methylotrophic bacteria	67	2.2×10^4	200
Ammonia oxidizers	55	3.8×10^1	566
Nitrite oxidizers	62	5.3×10^1	640

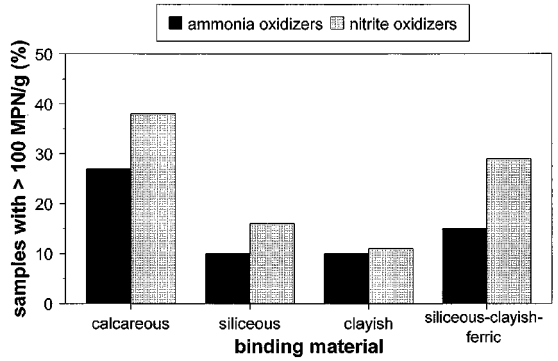

Figure 1. Frequency of nitrifying bacteria in natural stone with different binding material. Samples with cell numbers above 100 nitrifying units/g were counted.

geometric cell numbers of nitrifying bacteria, as determined by the MPN-test, were about a thousand-fold lower.

While chemoorganotrophic bacteria and fungi were found in more than 90% of the samples, nitrifying bacteria and facultatively methylotrophic bacteria were detected in less than 70% of the samples. Including only those samples in which the respective microorganisms were detectable (Table 2), the mean geometric cell numbers of nitrifying bacteria and facultatively methylotrophic bacteria were considerably higher: Average cell numbers of ammonia and nitrite oxidizers in colonized samples amounted to 3.8×10^1 and 5.3×10^1 MPN/g, respectively. Average cell numbers of facultatively methylotrophic bacteria in colonized samples amounted to 2.2×10^4 CFU/g.

The chemical/mineralogical composition and the pore-size distribution of the stone strongly influenced the colonization of natural stone with microorganisms. Nitrifying bacteria preferred calcareous stones (Figure 1) and a pH between 7 and 9 (not shown). Chemoorganotrophic bacteria and fungi preferred stone with siliceous-clayish-ferric binding material. Chemoorganotrophic bacteria were most numerous at neutral pH, whereas fungi were found in similar numbers over the whole pH-range. As previously published by Bock & Sand (1993), the highest cell numbers of chemoorganotrophic bacteria, fungi, and nitrifying bacteria were found in stone material with a medium pore radius between 1–10 μm. Microorganisms barely colonized material with a medium pore radius ≤ 1 μm, but, as Figure 2 shows, the colonisation by chemoorganotrophic bacteria and fungi was significantly higher in the presence of black crusts than without crusts. This was also the case for ammonia and nitrite oxidizers (not shown).

Surface samples of natural stone and mortar, taken from historical buildings in Eastern and Western Germany between 1990 and 1995, were compared. Mean values of chemical and microbiological parameters are shown in Figure 3. The mean geometric cell numbers of bacteria and fungi in samples from Eastern Germany were higher than in the western part of the country. The differences according to the U-Test for nitrifying bacteria and facultatively methylotrophic bacteria were statistically significant. As depicted in Figure 3, the mean geometric cell numbers of chemoorganotrophic bacteria and fungi in the eastern part of Germany were also higher than in the west, but this difference could not be verified by statistical methods. In addition the mean nitrite and sulphate contents in samples from Eastern Germany were significantly higher than in the west.

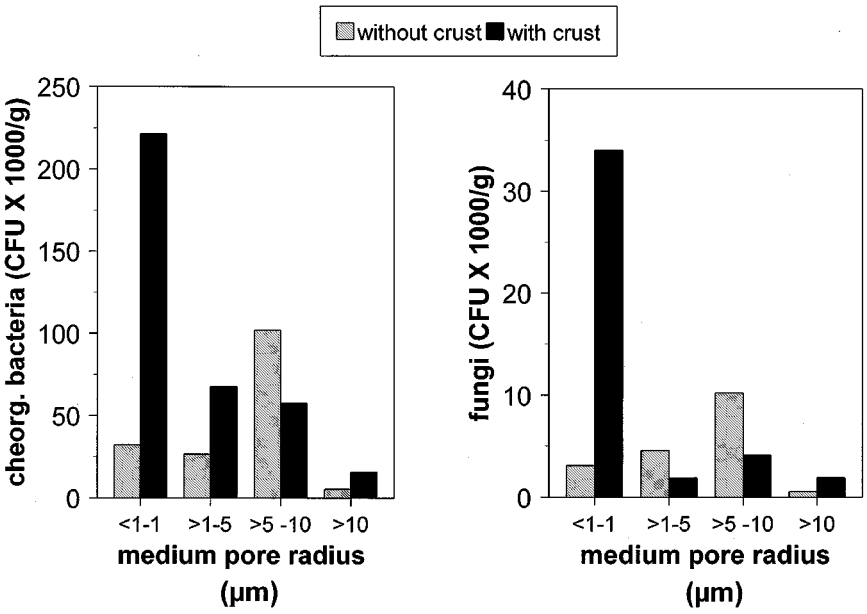

Figure 2. Influence of medium pore radius and black crusts on the colonisation of building stones by chemoorganotrophic bacteria and fungi.

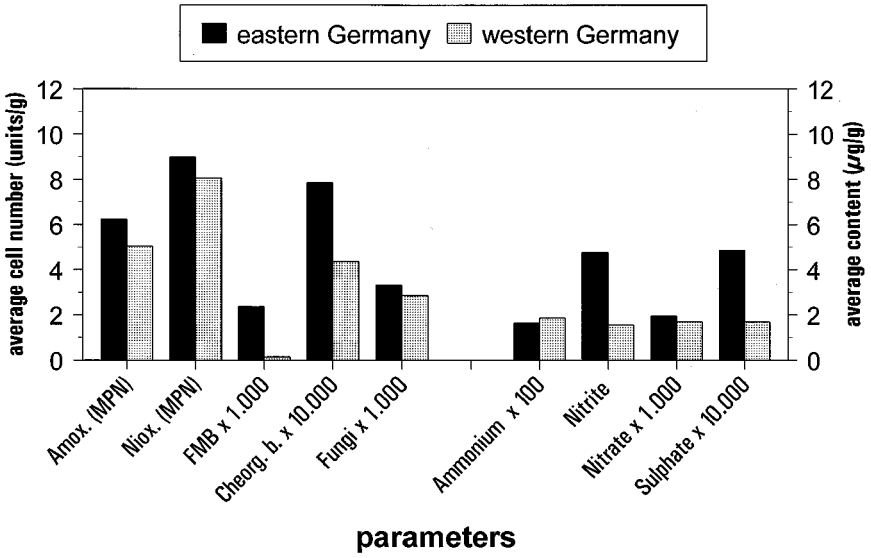

Figure 3. Comparison of chemical and microbiological parameters of natural stone and mortar samples taken between 1990 and 1995 from historical buildings in the western (n = 753) and eastern part (n = 314) of Germany. Cell numbers are expressed as geometric means (Y1-Axis) and chemical parameters as arithmetic means (Y2-Axis). Amox. = ammonia oxidizers; Niox. = nitrite oxidizers; FMB = facultatively methylotrophic bacteria; Cheorg. b. = chemoorganotrophic bacteria.

Outdoor exposure experiment (OEE)

Microbial colonization

As Braams (1992) and Warscheid et al. (1993) have reported before, within the first year, the specimens at both exposure sites were colonized with chemoorganotrophic bacteria and fungi. We detected nitrifying bacteria in surface samples (0–5 mm depth) from the Duisburg site (urban) for the first time in the second year of exposure. In the following years, nitrifying bacteria were only occasionally found in surface samples. Here we report the results of a thorough investigation performed in 1995 at both exposure sites. This time the sampling technique includes drill cores.

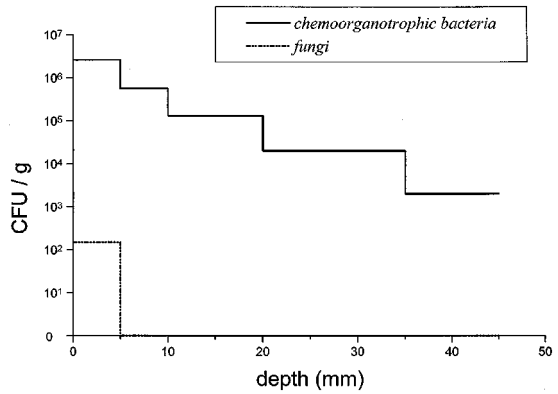

Figure 4. Typical distribution of chemoorganotrophic bacteria and fungi in a drill core from Ihrlersteiner green sandstone after exposure for 9 years in Duisburg (urban environment).

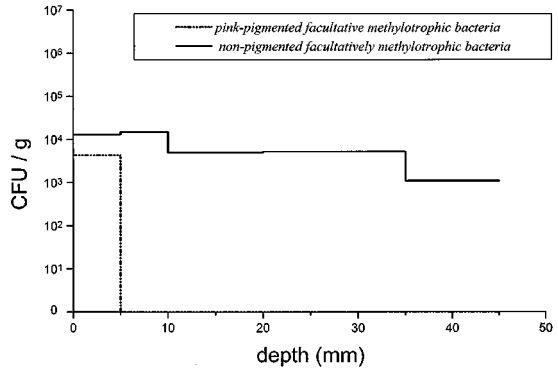

Figure 5. Typical distribution of non-pigmented and pink-pigmented, facultatively methylotrophic bacteria in a drill core sample of Ihrlersteiner green sandstone after exposure for 9 years in Duisburg (urban environment).

Mean geometric cell numbers of chemoorganotrophic bacteria for both materials were in the same range and did not significantly differ between samples from Duisburg (urban) and from Holzkirchen (rural). The cell numbers of chemoorganotrophic bacteria generally decreased with depth. Figure 4 shows a typical profile for Ihrlersteiner green sandstone (IG). For the Sander sandstone (SS), this effect was less pronounced (not shown). In both materials, fungi were limited to the upper 0.5–1.5 centimeters (Figure 4).

A typical profile of facultatively methylotrophic bacteria, as determined for IG in Duisburg, is shown in Figure 5, while Table 3 presents the geometric mean of all numbers. On IG and SS at both exposure sites, pink-pigmented facultatively methylotrophic bacteria (PPFM) were limited to 0.5–1.5 centimeters of depth (Figure 5). There was no significant difference in colonization with PPFM between the rural and urban site, but a remarkably stronger colonization by non-pigmented, facultatively methylotrophic bacteria was found in the Duisburg samples (Table 3). After 9 years, the IG in Duisburg was strongly colonized with nitrifying bacteria up to a depth of at least 5 cm (Figure 6). In contrast to the finding that the colonisation by chemoorganotrophic bacteria decreased with depth, the cell numbers of nitrifying bacteria in some cases even increased (core B, C, E). This was most pronounced for core C which represented the most significantly weathered site of the specimen. In Holzkirchen after 8 years of exposure (data not shown), ammonia and nitrite oxidizers were only found in core E (moist area). In core A (dry area), only nitrite oxidizers were detectable. Neither in Duisburg nor in Holzkirchen were nitrifying bacteria detected on SS.

Table 3. Mean geometric cell numbers of non-pigmented, facultatively methylotrophic bacteria in drill-core samples (0–5 cm in depth) of Ihrlersteiner green sandstone (IG) and Sander sandstone (SS) from urban and rural exposure sites

	Duisburg (urban)	Holzkirchen (rural)
IG	6.7×10^3	0.9×10^0
SS	1.6×10^3	8.9×10^1

Table 4. Mean arithmetic ammonium and nitrate contents of drill-core samples (0–5 cm of depth) from Ihrlersteiner green sandstone (IG) and Sander sandstone (SS) exposed at urban and rural exposure sites

	Duisburg (urban)		Holzkirchen (rural)	
	NH_4^+ (μg/g)	NO_3^- (μg/g)	NH_4^+ (μg/g)	NO_3^- (μg/g)
IG	0.8	52	6.5	67
SS	32	76	34	84

Ammonium and nitrate contents

Table 4 shows that the ammonium content of the two materials clearly differed. The enrichment of ammonium through deposition on the surface of SS (mean pH 6.4) was considerably higher than for the dolomitic IG (mean pH 8.1). Because the proportioning between ammonia and ammonium is shifted towards ammonium with decreasing pH, the enrichment of natural

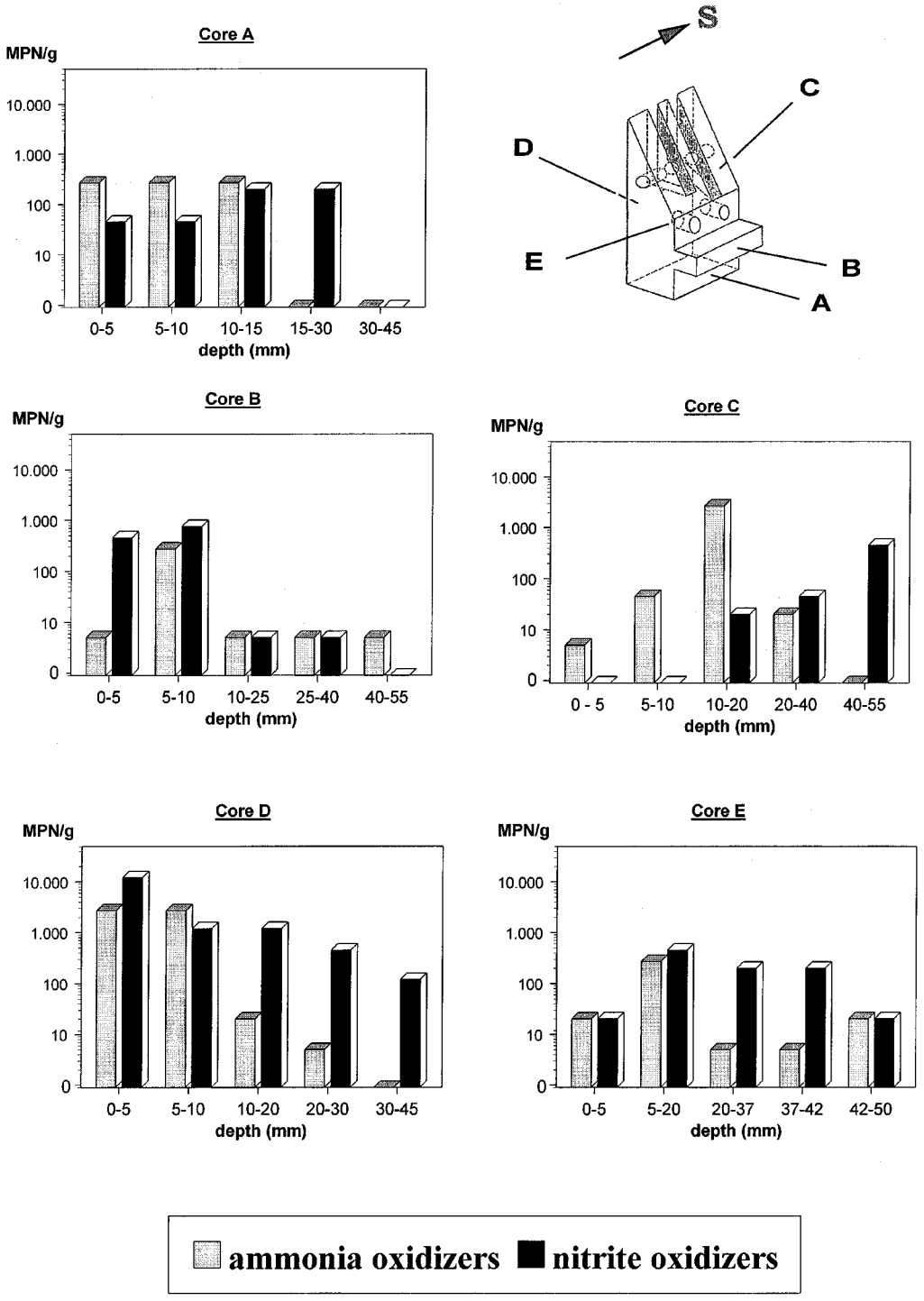

Figure 6. Cell numbers (MPN) of nitrifying bacteria in different depth of Ihrlersteiner green sandstone. Different positions were sampled by drilling (core ⌀ 22 mm) of one specimen (see drawing) after an exposure for 9 years in Duisburg (urban environment). → S = South.

stone with ammonium is negatively correlated to the pH (see Behlen et al. 1997 and previously published data of Bock & Fahrig 1993). Since the SS was not colonized by nitrifying bacteria, the ammonium content given in Table 4 represents the equilibrium between deposition and desorption. For the IG, especially in Duisburg, an additional consumption of ammonium and/or ammonia by nitrifying bacteria has to be considered (see below).

The mean nitrate contents, as given in Table 4, suggest that deposition of nitrate-forming compounds were roughly similar at both sites. High nitrate contents near the surface (about 500 μg/g maximum) were mostly found in areas of the specimen that were dry.

Denitrification

Only surface samples originating from 0–5 mm of depth showed a denitrifying potential (> 60% nitrate removal). Nitrite appeared as an intermediate in the tests. With one exception (SS from Holzkirchen), all samples with denitrifying activity originated from the IG at Duisburg. Mean arithmetic cell numbers of chemoorganotrophic bacteria and fungi, according to the U-Test, were significantly higher in surface samples with denitrifying activity (n = 7) compared to surface samples without (n = 7). Numbers of facultatively methylotrophic bacteria were not significantly different.

Laboratory simulation experiments

A high stone moisture was essential to establish a nitrifying microflora on test-blocks from the dolomitic Ihrlersteiner green sandstone (IG). In a long-time simulation experiment (40 weeks), interactions between chemical and microbiological weathering were demonstrated for the first time. The formation of gypsum from sulfur dioxide was enhanced in the presence of nitrifying bacteria. In the presence of sulfur dioxide, the biogenic nutric acid attack was strongly reduced through chemodenitrification of nitric acid. The results summarized in the preceding as well as the experimental setup and chemical data were described before by Mansch & Bock (1996).

Previously unpublished data from two long-time simulation experiments, which are part of dissertation by Mansch (1994), are presented in the following. In Figure 7, the MPN cell numbers of nitrifying bacteria (0–5 mm depth) in specimens from IG inoculated with nitrifying bacteria and exposed to a simulated smog atmosphere (1065 μg/m^3 SO_2, 850 μg/m^3 NO and about 450 μg/m^3 NO_2) are depicted. The mean arithmetic cell numbers of ammonia and nitrite oxidizers were 1×10^7 and 4×10^7 cells/g, respectively. For the first 9 weeks, the specimens were exposed to ambient air. After exposure to the simulated smog atmosphere, the cell numbers of ammonia and nitrite oxidizers decreased by a factor of 10 to 100 times, respectively. The same was true for the potential nitrification activities (not shown). After this temporary decrease, cell numbers and activities steadily increased in the presence of the complex gas atmosphere. Cell numbers of ammonia oxidizers increased from 4.5×10^5 cells/g (week 15) to 8×10^6 cells/g by the end of the experiment (week 40). Cell numbers of nitrite oxidizers in the same period increased from 3×10^6 to 5×10^7 cells/g. The values of the potential nitrification activities followed this trend and, by the end of the experiment, were for ammonia oxidizers 1.4 times and for nitrite oxidizers 2.3 times higher than in the beginning (not shown). Cell numbers and potential nitrification activities of specimen constantly held in ambient air did not increase during the experiment, but fluctuated around a mean value (data not shown). Similar results were found in a second long-time experiment (29 weeks) with IG.

Discussion

Chemoorganotrophic bacteria and fungi

The most numerous microorganisms in natural building stone are chemoorganotrophic bacteria. Results of Braams (1992) and Warscheid et al. (1993) indicate that they colonize natural stone within weeks. Therefore, it is likely that many of the stone inhabiting chemoorganotrophic bacteria are so-called oligotrophs, being capable of living from the small amounts of nutrients supplied through the atmosphere (Wainwright et al. 1993). Nevertheless, the significantly higher cell numbers of facultatively methylotrophic bacteria at the urban exposure site of Duisburg and on buildings in Eastern Germany indicate that high emissions of organic pollutants may enhance the development of some groups of chemoorganotrophic bacteria. While pink-pigmented facultatively methylotrophic bacteria (PPFM), which as common airborne organisms are frequently found on leaves (Green 1992), were present in similar numbers at both exposure sites, non-pigmented, facultatively methylotrophic bacteria were found in significantly higher

cell numbers at the urban site (Duisburg). The non-pigmented methylotrophic bacteria include different genera with the ability to use several one-carbon and multi-carbon compounds. As Nord et al. (1994) found, natural building stone in urban environments was significantly enriched with organic components originating from combustion of petroleum products. Reports of Warscheid et al. (1991) and Saiz-Jimenez (1993) support the assumption that growth of chemoorganotrophic bacteria on natural stone is favoured by deposition of hydrocarbons. We conclude that the high level of anthropogenic air pollution in Duisburg and in the eastern part of Germany (Steiger et al. 1993; Anonymous 1992) caused high cell numbers of facultatively methylotrophic bacteria on natural stone.

For several reasons it is difficult to assess the importance of a strong colonization with chemoorganotrophic bacteria to the biodeterioration of building stone. Although some acid-producing strains have been isolated (Palmer et al. 1991), there is still little evidence that direct weathering by excretion of organic acids and/or production of carbon dioxide by chemoorganotrophic bacteria can be a relevant weathering mechanism *in situ*. Nevertheless, there is no doubt that the massive growth of chemoorganotrophic bacteria in building stone has negative effects on the material. Biofilm formation and discoloration have to be mentioned (Warscheid et al. 1993; Warscheid & Krumbein 1996). High cell numbers of chemoorganotrophic bacteria show favourable conditions for other microorganisms, like fungi and nitrifying bacteria, and therefore indicate a potential endangerment of the material by biodeterioration.

Mean geometric cell numbers of fungi in building stone were about 100 times lower than cell numbers of chemoorganotrophic bacteria. Our results are in accordance with reports of other authors, who state that the colonization of natural stone with fungi follows the colonization by chemoorganotrophic bacteria (Braams 1992). A strong colonization of building stone by fungi is potentially endangering the material, as the weathering of natural stone by organic acids excreted by fungi has been demonstrated in several investigations (Henderson & Duff 1963; Eckhardt 1979; De la Torre et al. 1993a).

Stone characteristics

The pore-size distribution, as well as the chemical/mineralogical composition of a natural stone, strongly influences the colonization by microorganisms.

The highest numbers of chemoorganotrophic bacteria, fungi, and nitrifying bacteria were found in stone material with a medium pore radius between 1–10 μm. Pores of this size can easily be invaded by microorganisms in moving water, and they have a good water-holding capacity. Larger pores allow a more rapid evaporation and thus rapid drying of the stone. Pores smaller than 1 μm in diameter cannot be colonized by most microorganisms. Thus, stones with a high proportion of pores ≤ 1 μm were scarcely colonized with microorganisms. As our results show, this situation changes drastically if crusts are formed on the stone material. We conclude that the physicochemical conditions, e.g., pore size distribution and moisture conditions, in and under a crust are more favourable than without a crust. Microorganisms adsorbed to particles entrapped into the crust contribute to higher cell numbers. In this sense, the formation of black crusts by chemical processes like sulphation and deposition of dust and organic particles (Saiz-Jimenez 1993; Nord et al. 1994; Sabbioni 1995) make way for a strong colonization by microorganisms.

Although chemoorganotrophic bacteria were most numerous in material with a siliceus-clayish-ferrous binding material and neutral pH, these organisms, in contrast to nitrifying bacteria, did not have very strict requirements with respect to stone characteristics. The same was true for fungi. Consequently, chemoorganotrophic microorganisms were present in almost every sample.

Nitrifying bacteria

Our results on colonization of natural stone by nitrifying bacteria exhibit remarkable differences in respect to chemoorganotrophic bacteria and fungi. The colonization of natural stone by nitrifying bacteria is a slow process. The requirements of nitrifying bacteria concerning stone characteristics are more specific, and it is unique to nitrifying bacteria that the highest numbers may be found underneath the surface.

The mean geometric cell numbers, as determined with the MPN-method, are about 1000 times (Table 2) lower than cell numbers of chemoorganotrophic bacteria. However, the MPN-method severely underestimates the cell numbers of nitrifying bacteria as it has a counting efficiency of less than 5% (Belser & Mays 1982; Cooper 1983). One reason is that nitrifying bacteria living in microcolonies will be counted as

a single nitrifying unit, while another is that growth media may select for certain subpopulations (Cooper 1983; Both et al. 1990; Underhill 1990). The results from the exposure sites, as well as findings of Bock (1987), show that nitrifying bacteria frequently colonize deeper sections of building stone, and, thus, surface samples (0–5 mm) mainly taken from buildings may underestimate a colonization with these bacteria.

Initial colonization of natural stone by nitrifying bacteria takes several years. Among the factors dictating whether a material is colonized by nitrifying bacteria are the availability of pores of a suitable size (1–10 μm radius), a pH in the range between 7–9, and a sufficient buffering capacity (dolomitic/calcareous binding material). LSE demonstrated that the Ihrlersteiner green sandstone is a material that well supports the growth of nitrifying bacteria (Mansch 1994). Nevertheless, after 8 years, the material at the rural exposure site of Holzkirchen was only scarcely colonized. In contrast to that finding, under urban conditions (Duisburg) and after an exposure of 9 years, the specimens were strongly colonized with nitrifying bacteria up to a depth of 5 cm. This difference did not result from nutrient limitation at the rural exposure site of Holzkirchen, as the ammonium contents of the IG in Holzkirchen were even higher than the values from Duisburg (Table 4). Instead, it is likely that the IG at the rural site was still too alkaline to become readily colonized with nitrifying bacteria. As results from laboratory simulation experiments indicate, an acidification of calcareous material favours the colonization with nitrifying bacteria (Mansch 1994). Therefore, we assume that at the Duisburg site, in contrast to Holzkirchen, the strong chemical weathering by sulphur dioxide and other components of anthropogenic air pollution initiated and enhanced the colonization of IG with nitrifying bacteria.

This conclusion is strongly supported by results from the LSE reported here for the first time. As Figure 7 demonstrates, growth of nitrifying bacteria on Ihrlersteiner green sandstone was enhanced by a simulated smog atmosphere containing NO, NO_2, and SO_2. The first and most important explanation for this finding is that freshly quarried dolomitic or calcareous stones have a pH near 9. This value is at the upper limit of the suitable growth range and considerably higher than the optimal pH of 7.8 reported for growth of nitrifying bacteria in liquid culture (Koops & Möller 1992; Bock & Koops 1992). Chemical weathering, especially by sulfur dioxide, lowers the surface pH of the stone and causes a pH gradient inside the material. By this gradient, optimal conditions for growth of nitrifying bacteria are achieved. Additionally, nitrogen oxides may have contributed to the positive effect of the simulated smog atmosphere on nitrifying bacteria. Results of Schmidt (1997) and Zart & Bock (1998) indicate a positive effect of nitrogen dioxide on the growth and activity of ammonia oxidizers, while Mansch (1994) and Vollmer (1997) demonstrated that nitrite oxidizers can oxidize nitric oxide to nitrate.

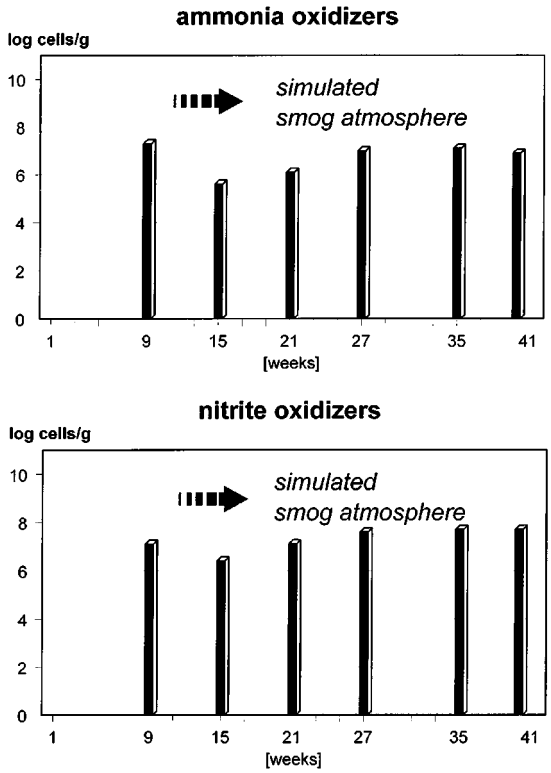

Figure 7. Cell numbers of ammonia and nitrite oxidizers from the first 5 mm of sealed specimen (5 × 5 × 30 cm) of Ihrlersteiner green sandstone. After 9 weeks in ambient air the samples were exposed to a simulated smog atmosphere (1065 $\mu g/m^3$ SO_2, 850 $\mu g/m^3$ NO, about 450 $\mu g/m^3$ NO_2). The specimens had been inoculated with nitrifying bacteria at the beginning of the experiment and were incubated under optimal conditions in a controlled climate chamber.

The assumption that nitrifying bacteria prefer to grow in a pH-gradient is also supported by data from Wilimzig & Bock (1996). High cell numbers underneath the stone surface, as shown in Figure 6, may therefore indicate the difference between strongly weathered and more intact stone material. Core C from the IG at the Duisburg site, which originated from the most strongly weathered position of the specimen (Figure 6), may support this assumption. We suspect that, after initial colonization, the acid-producing

ammonia oxidizers themselves contribute to the acidification and weathering of the stone. If strong chemical weathering is missing, as in Holzkirchen, the colonization of calcareous material with nitrifying bacteria proceeds rather slowly. At the rural site in Holzkirchen, only a moist part of the specimen was colonized with nitrifiers. This finding indicates that sufficient stone moisture is another important factor for the colonization of natural stone with these bacteria. This assumption is strongly supported by empirical knowledge gained from many buildings and by observations of Wilimzig (1996) and Jozsa et al. (1996a). On the one hand, the relatively low pH (mean value 6.4) prevented the SS from being colonized by nitrifying bacteria at both exposure sites. On the other hand this pH value leads to a comparatively strong enrichment of ammonium (Table 4). Therefore a high ammonium pool seems not to support the growth of nitrifying bacteria, unless the pH of the material is in a range suitable for cell growth. In natural stone the highest cell numbers of ammonia oxidizers were found between pH 7.5 and 9.0 (Fahrig 1991). In contrast to the experimental situation, a stone block in a wall of a building is usually surrounded by an alkaline mortar providing a buffering capacity. Under these circumstances, even materials like SS were found to be colonized with nitrifying bacteria, especially those parts close to a mortar joint (Wilimzig & Bock 1994; Bock et al. 1994). These observations should be taken into consideration when the results from OEE are interpreted with respect to the situation of a building.

The finding that calcareous material with a low ammonium content was deeply colonized by high numbers of nitrifying bacteria, as was the case in Duisburg, leads to the question how ammonia oxidizers are supplied with their substrate. It is well known that ammonia, not ammonium, is the real substrate for ammonia oxidizers (Suzuki et al. 1974). Therefore, ammonia may reach the bacteria inside the pore space through the gas phase. If ammonia oxidizers in natural stone live from ammonia rather than ammonium, the availability of their substrate is closely linked to the pH: e.g., at pH 7.4 about 1% of the ammonium pool is available as ammonia. Therefore materials with a pH < 7 usually build up a relatively high ammonium pool through dry and wet deposition from the atmosphere (Behlen et al. 1997), but little of this potential substrate may be available for ammonia oxidizers. Alkaline materials with pH > 7 accumulate a rather small pool of ammonium, but may constantly supply ammonia to the nitrifiers. The results presented in this paper suggest that not the absolute ammonium content of building stones, but the availability of ammonia is the crucial point for endolithic growth of nitrifying bacteria. This hypothesis is in agreement with the empirical finding that in LSE on alkaline materials with small ammonium pool high cell numbers and activities of ammonia oxidizers were achieved (Mansch 1994).

Although nitrifying bacteria are not the most numerous organisms in building stone, their strong weathering potential as demonstrated by LSE (Bock et al. 1989; Mansch & Bock 1996) and their unique ability to deeply colonize natural stone, are indicative of their importance in biodeterioration.

Nitrate in building stone

Surprisingly, the strong colonisation of IG by nitrifying bacteria at the urban exposure site (Duisburg) was not reflected in the nitrate content of the specimen (Table 4). The same was true for data from buildings evaluated by Bock & Fahrig (1993). The authors found that according to a Spearman rank correlation analysis, there was no correlation between cell numbers of nitrifying bacteria and the nitrate content of samples. Nevertheless, a highly significant negative correlation between the protein content and the nitrate content existed. In addition, it could be verified that a negative correlation between cell numbers of chemoorganotrophic bacteria, along with fungi and the nitrate content, existed. These findings point to the fact that nitrate in building stone may be consumed microbiologically, most likely by denitrification. The finding that the stone inhabiting denitrifying microflora in samples from the urban exposure site of Duisburg was able to cause a significant reduction in nitrate content indicates that in an urban environment the enrichment of natural stone with organic substances (Nord et al. 1994) may be sufficient to support denitrification. Therefore, we assume that a nitrate loss through biological processes has to be taken into consideration when the nitrate load of building stones is evaluated, especially in the presence of a strong colonization by chemoorganotrophic bacteria and fungi. Anaerobic to microaerophilic conditions, as needed for denitrification (Lloyd et al. 1987; Tiedje 1989), are most likely to occur during phases of high stone moisture.

Nitrate in building stone can also originate from deposition of nitrate and/or reactions of nitrogen oxides with the stone material. As nitrifying bacteria

were absent on SS at both exposure sites, the nitrate in this material is of chemical origin. In addition, nitrates are highly mobile salts. Consequently, the site of nitrate formation/deposition is not necessarily identical with the one where high concentrations of these salts are present. For these reasons, nitrate is a rather insecure parameter to reflect the endangering of a building by nitrifying bacteria.

In contrast to nitrate, sulphate in building stone is biologically stable and has a low solubility. Therefore the enrichment of building stone with sulphates (mainly gypsum) gives a record on the weathering by sulfur dioxide during a building's history. This correlation is reflected in the high mean sulphate content of samples taken from buildings in eastern Germany (Figure 3). As the differences in formation and behavior of nitrate and sulphate in building stone show, a comparison of the amount of nitrate and sulphate found in the material does not necessarily indicate the importance of the respective weathering processes.

Conclusions

Our results indicate that anthropogenic air pollution and its results, including enrichment by organic substances, formation of crusts, and chemical weathering, promotes the colonization of natural stone by microorganisms and thus enhances biodeterioration processes. Consequently, chemical and microbiological weathering can neither be strictly separated nor separately evaluated.

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