

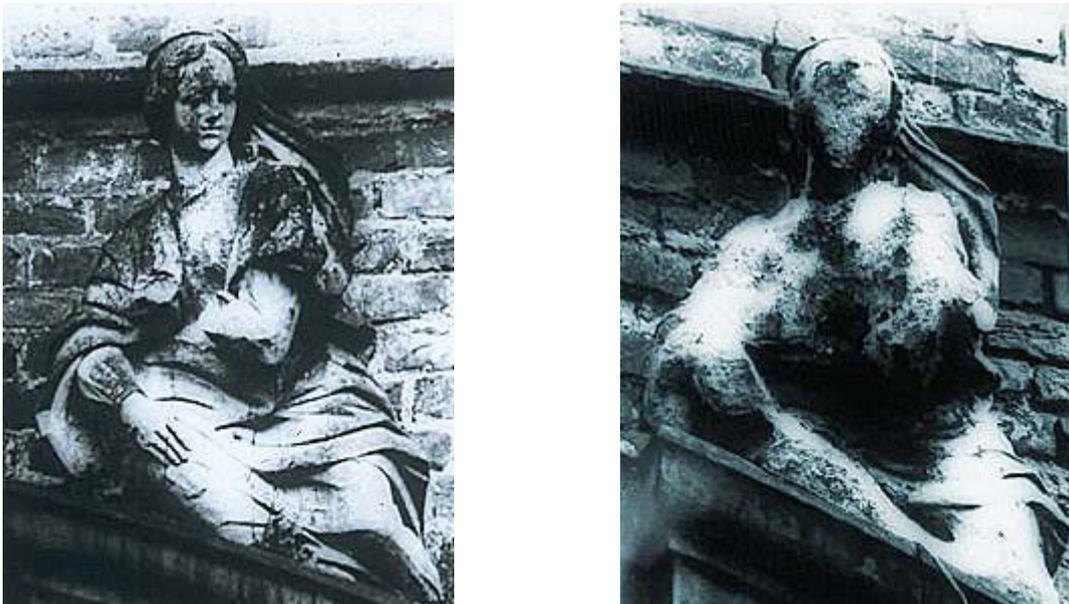
# Saving Cultural Heritage in Germany

## A Spotlight on the Present Situation at the Beginning of the New Millennium

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### 1. Introduction

Restorers and art historians who were working with architectural monuments in the 1960ies observed that many historic monuments seemingly deteriorated at a much higher rate than it should have been expected only by natural ageing. This effect could be visualised impressively in comparative studies of documents that showed the preservation state of some monuments at the beginning of the 20<sup>th</sup> century and approx. 60 years later.



*Fig. 1: Sculpture from Herten Castle (dated about 1750) showing the progress in stone decay during the last century. The left photograph is from 1908, the right one from 1969*

It was concluded that if there will not take place dramatic changes to the quality of the atmospheric environment - which was supposed to be the main cause of the observed changes - we will loose by the end of the century a substantial part of our cultural heritage. In 1975 Feilden estimated that by the end of the century only 10% of the architectural heritage will “survive”, 1989 he gave a more “optimistic” estimation, saying that hopefully it will be more than 20% (1). To a similar conclusion came Winkler 1973 (2), who included results of many different studies on stone deterioration (time lapse) into a diagramme, where can easy be recognized that most of the stone surfaces should be strongly deteriorated by the end of the 20<sup>th</sup> century.

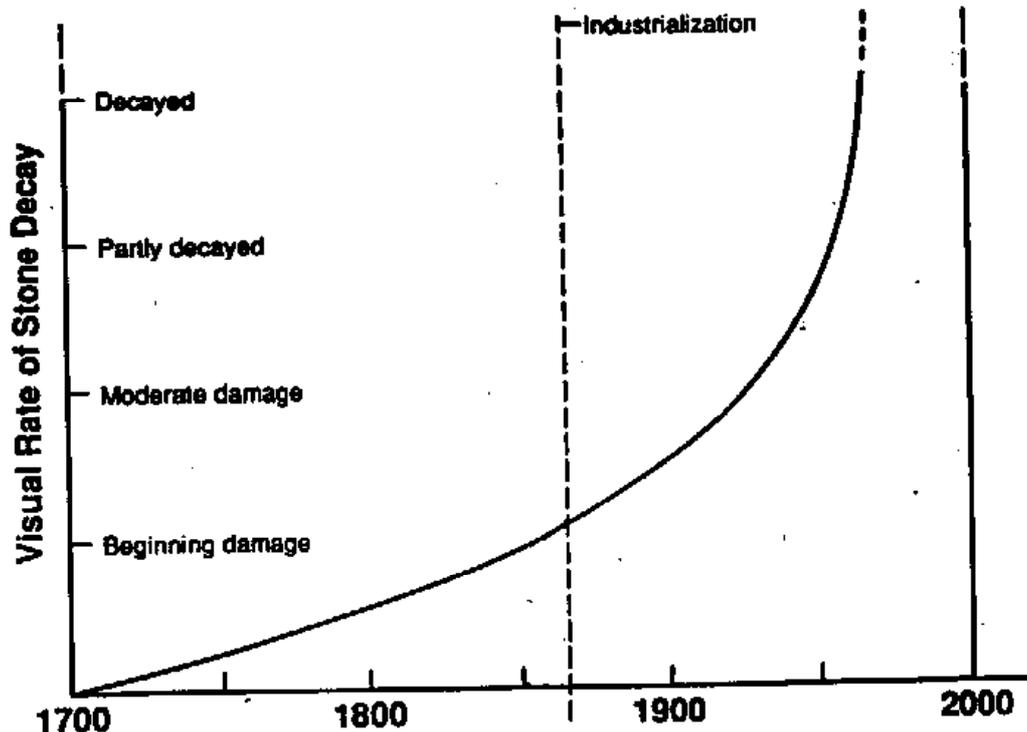


Fig. 2: Stone decay rate plotted against the age of stone objects (after Winkler 1973)

Similar results can be reported also from different materials, as for instance for medieval stained glass windows (3) or historic bronze sculptures (4).

## 2. Today's situation

Now, at the moment where the magic year 2000 has passed, we learn that the present state of preservation of historic monuments is much better than the predictions once stated. However, does that mean that the predictions were incorrect? Were they based on wrong assumptions or were the meanwhile undertaken counteractions, successful enough to stop or to slow down the processes of deterioration? There is no simple answer now to give.

Let's go back into the 1960ies. The main hypothesis that was used to explain the observed accelerated decay of cultural materials is based on the effects of air pollution, namely of sulphur dioxide and of "acid rain". Both "pollutants" increased their concentration in the atmosphere since the beginning of the industrialisation in the 19<sup>th</sup> century. It was therefore deduced that they are responsible for the damage. At this point it is important to clarify that the main subject of concern were not the historic heritage objects, but human health and (as we say now) forest ecosystems. Some years later also surface water and soil were recognised as endangered by acidification due to acid deposition.

To avoid further damage resp. to reduce the risk to loose heritage, two main strategies were followed:

- a) protection of all objects that were affected by environmental stress either by improvement of the material properties or even replacement with more resistant materials (= passive protection).
- b) abatement of the possible causes of deterioration, that means the reduction of the emission of acid gases from different sources (= active protection).

Without any doubt, both strategies have to be applied, but there are substantial differences, how these goals can be achieved. Necessary prerequisite for the first strategy is the precise knowledge of the processes leading to decay. The second way – the reduction of pollution – is mainly driven by economic considerations. At the end both strategies should lead to a unified way, how to improve the state of the environment and to reduce the risk of damage to cultural heritage at a minimum.

## **2.1 Understanding the mechanisms of decay**

It was well understood, that scientific research is necessary to understand better the processes of deterioration of materials and also to develop methods for rehabilitation and conservation of the endangered heritage. Measures initiated on pure empiric knowledge are certainly a good prevention, but they do not guarantee success. On the other hand pure scientific research gives clear results, however often fails, when applied in practice.

The main achievement of the years lying now behind us, was the creation of an interdisciplinary cooperation of all persons and bodies that integrated both – science and practical experience. I think that the most important new views on the problem are based on a methodological way of working with the problem. For the first time many different disciplines from science, humanities, architecture, engineering and others came together and tried to find solutions for problems that in the past were thought to be problems only of one of these groups respectively. This cooperation needed several years of intensive exchange and discussions and it seems that it started to work now.

It is not possible to give here an overview of all activities and achievements that have been done in Germany for the protection of historic monuments and the specific research for a better understanding of their decay processes. I therefore pick up only one example – stained glass windows – and will explain for this case how the problems were handled. Evidently the whole variety of historic building structures and other monuments consisting out of a variety of stone material, metals, brick structures and many other different cultural materials do behave in their environment differently in detail. However, in this one typical example can be shown that in principle there are great methodological similarities in respect to the ways, how to make progress in conservation, which are valid for all materials.

## **2.2 Example: Stained glass windows**

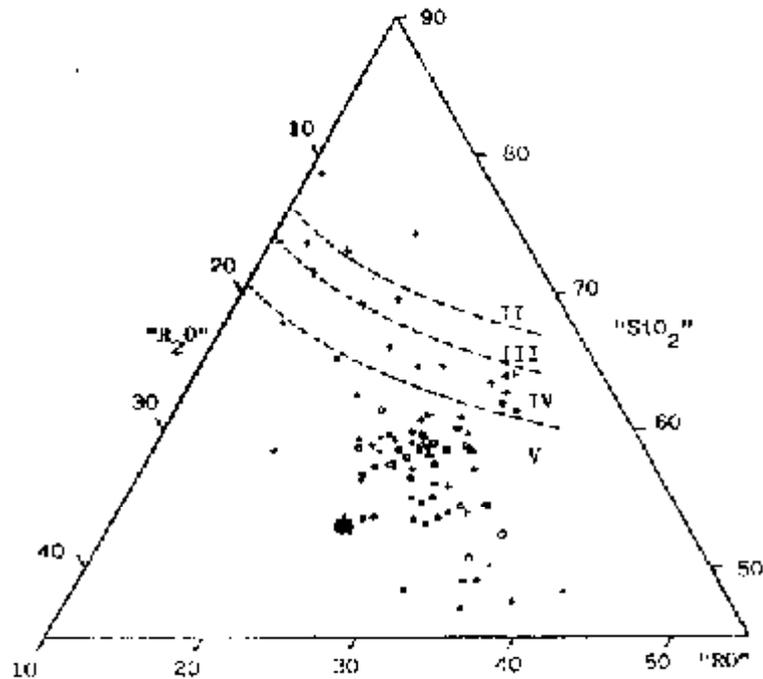
Stained glass windows are works of art that have been created mainly in the medieval ages in Europe. From the beginning of the 19<sup>th</sup> century they came into use again worldwide. They are made of differently shaped pieces of coloured glass held together with a net of lead profiles. The transparent glass gives the window a colour pattern, while the leads contribute to the main profiles of the intended drawing. The glass surface is painted with a black stain – a pigmented glass flux burned into the surface of the transparent glass – and is responsible for details of the representation. In their function as windows of medieval cathedrals and churches they were exposed to direct atmospheric influences since hundreds of years.

### **2.2.1 Mechanisms of decay**

In the past the damage to glass surfaces were described only phenomenologically. Different types of damage, such as formation of weathering crusts, surface recession, pitting, darkening, crizzling of surfaces and many others were observed on historic glasses. The degree of decay of individual pieces of glass also very different, even within one stained glass window.

One of the main reasons of these undesired processes are to be found in the material itself (intrinsic causes of decay): Depending on its individual composition, glass can be a very sensitive material in respect to chemical attack, both alkaline or acidic. Depending on the chemical composition of glasses a rough prediction of its resistivity against chemical attack is possible. For historic glass this knowledge allows to define the individual risk of damage. A graphic representation of the main components of glass in a triangular diagramme allows to distinguish between those that are durable and those that are highly corrodible.

## Composition of medieval glass



### II, III, IV and V - regions of hydrolytic classes

- + - glass without corrosion
- o - glass with pitting corrosion
- - glass with uniform corrosion
- \* - composition of synthetic glass type M I

Fig. 3: Composition of medieval glass represented in a triangular diagramme and its stability against acid attack (hydrolytic classes)

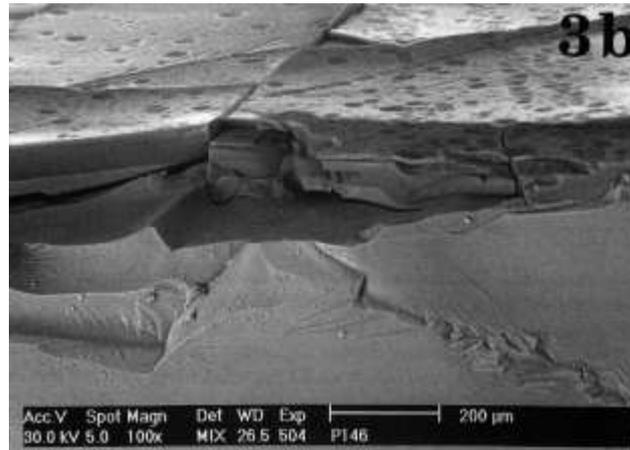
The evaluations of the extrinsic causes for the decay were more important, as they opened the chance to more active protection strategies. In the first years of research devoted to stained glass corrosion there was a scientific controversy, whether air pollution, namely sulphur dioxide is the cause for the observed accelerated damage or not (5). Undoubtedly the alteration (or corrosion) products found at the glass surfaces was gypsum and to some smaller extent another low soluble salts of sulfuric acid. How they were formed, or where did they come from?

Scientific research of the past 30 years in this field brought much light into the understanding of processes affecting the historic glass surfaces. We are now at a point where we do understand most of the effects at least in qualitative terms. Without going into all details of atmospheric corrosion of glass, the basic principles should be briefly explained so far they are understood up to now.

The surface of a freshly produced glass that comes into contact with the natural atmospheric environment is covered by a thin film of water. The thickness of this invisible layer may vary from only a few molecules  $H_2O$  up to layers of some hundred molecules, depending on the humidity content of the environment (usually given as RH) which is in contact with the surface. This water layer has two functions: it reacts with the glass and it is solvent for compounds deposited from the environment.

The first reaction results in formation of silica gel layers which cover the glass surface. They are mainly composed of hydrated silicium dioxide and may contain low concentration of other cations. The chemical reaction behind this conversion is a cation exchange of protons

contained in the water layer against alkaline and earthalkaline ions, which are main components of alkaline-silica-glasses.



*Fig. 4: Scanning electron micrograph of an edge of a corroded glass, showing the corrosion and silicagel layer on top of the bulk glass.*

The kinetics of this reaction strongly depends on diffusion processes between liquid-solid phases and within solid phases. In more “open” glass structures the mobility of ions is higher than in the denser ones. The structural glass model by Zachariasen allows to understand that mainly medieval glasses, which contain high amounts of potassium (modern glasses, but also those from antiquity contain sodium as one of the main components) have very “open structures” and are therefore extremely susceptible to cation exchange reactions. This explains also that in humid environment the degree of the cation exchange is forced more than under more dry conditions. The formation of a gel layer between the outer surface (that one in contact with atmosphere) and the bulk glass has the effect of slowing down the corrosion process.

The second type of reaction that takes place at the glass surface depends on the chemical composition of the surface water layer. The sources of ions in this layers are the glass matrix itself (extracted cations from the glass matrix), alteration products from previous reactions (weathering crusts, “patina”) and depositions from atmosphere (gaseous, wet or solid). Obviously acid deposition has strong influence on the ongoing reactions in this surface layer and it is also clear that only insoluble (or low soluble) salts are found at the surfaces as precipitation products. Nitrates and chlorides were not found in solid corrosion products.

In this context it is also important to mention that water on the surface is a media necessary for biological activity. It could be shown that microorganisms are able to live on glass surfaces and can contribute to their alteration.

### **2.2.2 Conservation – Restoration – Prevention**

In the second half of the 19<sup>th</sup> and until the middle of the 20<sup>th</sup> century and many different efforts were undertaken to restore the weathered stained glass windows that have lost partially their transparency. Replacement of the weathering crusts (cleaning), often by rather tough methods such as abrasion of the layers, or etching with acid were the prevailing methodologies. In some cases surfaces were “protected” by application of different lacquers (for instance epoxides, which are yellowing meanwhile). Finally a substantial part of the original glasses were replaced by modern copies. This is not in agreement with modern conservation ethics! With this background and the modern understanding of conservation – that means the preservation of the original – the conservation research focused on following tasks:

- Which possibilities are available for the replacement of weathering crust (and previous restorations), without substantial alteration of the original surface of the glass and the paint?
- Which methods of stabilisation of the present status we have, without causing new problems on long term?

Based on the knowledge of the corrosion mechanisms of glass, the structure of the surfaces (also the altered ones) we know now, which possibilities of cleaning surfaces are available, without substantial additional damage to the glass. The silica gel layer that covers the bulk glass matrix has to be preserved under all circumstances. The methods range from very conservative mechanical cleaning with a brush to microblasting, application of chemicals in compresses and in a very limited extent to cleaning with lasers. All of them need well educated and trained restorers. For some special cases of damage, as for instance the darkening of windows, which is now well understood as an oxidation process of manganese in the glass surface, hydrazine reduction leads to success. Windows treated in that way regain their transparency. Approximately 20 years of research has been invested to proof all possibilities of eventual failure in this case.

For the preventive conservation and protection of historic glass two strategies have to be followed in the future, both based on the knowledge that weathering can be avoided when high humidity and air pollutants are kept away from the glass surface.

One possibility could be the application of coatings which can protect the glass surface from direct contact with all compounds that contribute to weathering processes. However, most of the available products on the market do have only short term protective properties. They are also subject of ageing process by themselves and can lead to stronger damage when applied as if their application would not have taken place. Extensive tests carried out over a period of several years have shown that best available coatings are acrylic resins (Paraloid B72) and ORMOCER® coating (organic modified silicates).

The second and more often used possibility for the protection is an external glazing. This is a constructive solution of the problem and improves the direct atmospheric environment of the glass. The most important advantage of this protective system is that the original windows do not need to be touched. Although the idea of external glazing is not new, only in recent times a systematic investigation of all parameters that may influence the efficiency of this protective method were performed. The outcome of these efforts are ideas how to design the construction details in a variety of different types of external glazing, each optimised and adapted to the individual situation of the windows that should be protected. Nevertheless, with an external glazing the original appearance of the buildings is changed – in so far this type of protection is still a compromise solution of a problem which needs further attention.

### **2.2.3 Education – training – public awareness**

It became clear during the last years of dealing with the problems of heritage conservation that this is not only a problem of physico-chemical processes, resp. of their prevention, but has roots also in the lack of communication between the owners, curators, architects, restorers, craftsmen and scientists. It turned out that many of scientific and technical solutions for a better protection could not be applied, because they would cause unsurmountable problems for conservation ethics.

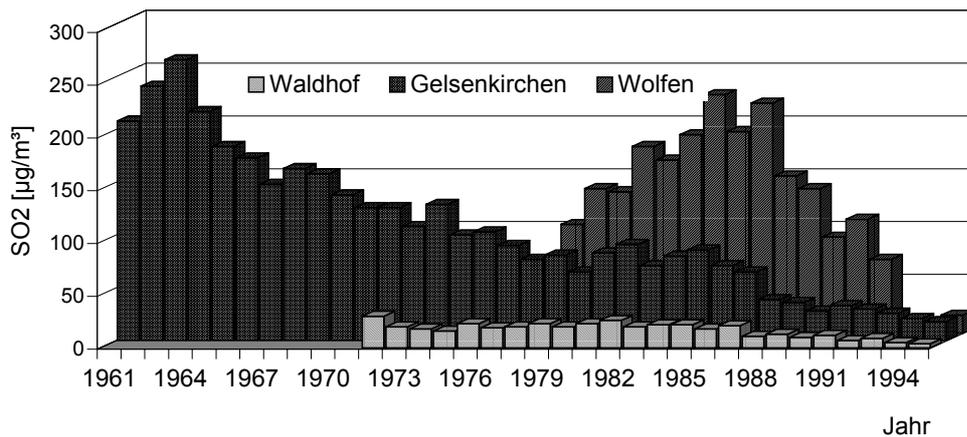
Seen in this light one of the most important achievements of the recent conservation research work was the beginning of real cooperation and dialogue between the different involved disciplines. This is meant really as a cooperation, not only as some verbal statements which in fact were not filled with action. Probably far more important has been the fact that involvement of persons, who are responsible for the practical work – both craftsmen and restorers – into most of the stages of scientific research, have qualified them for extremely good results. Training courses, discussions in workshops and directly at the objects are very efficient and guarantee sustaining results of undertaken measures.

It has to be added that the effectivity of all actions to save cultural heritage from decay can be only successful when it is backed by general public awareness (not only that of an elite) to the problem, because all actions need both - political and economic support. Those are available only when a strong pressure group stands behind and when they are socially accepted.

### 2.3 Reduction of environmental stress

Active protection, i.e. the reduction of the air pollution was - in the first years after the problem was recognised as such - mainly driven by legislative rules within national borders and also by international treaties, as for instance by the protocols ratified by several countries within the UN ECE Convention on Long-range Transboundary Air Pollution (LRTAP) (<http://www.unece.org/env/lrtap/>).

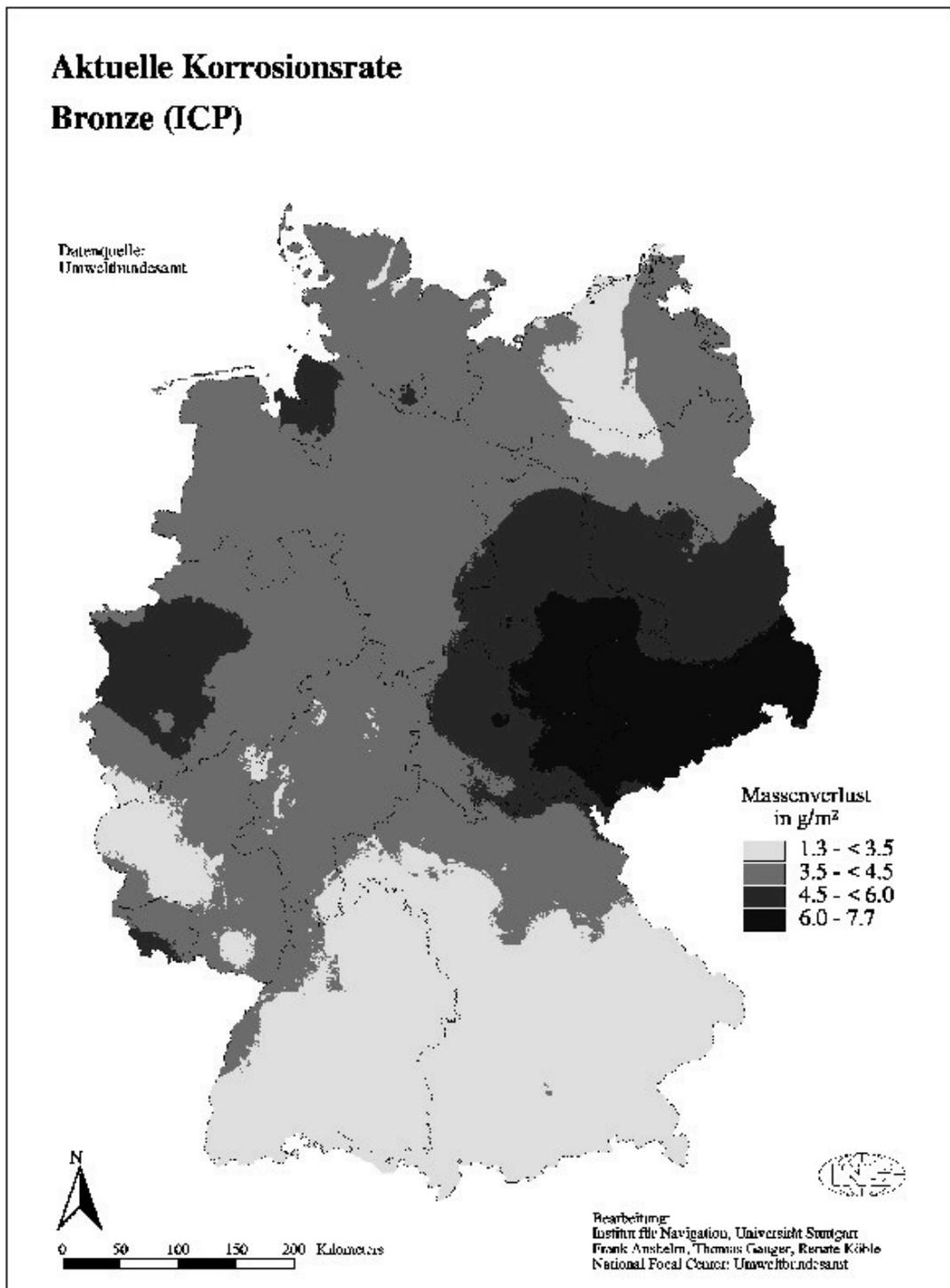
Based on the hypothesis that damage to vegetation, ecosystems, surface waters, soil and materials is mainly caused by pollution effects, the political will was therefore to counteract in reverse: with a general reduction of air pollution levels in the environment the damage was expected to be reduced too. In the first years the only determining actions were to reduction of emissions as far as it was possible. The determining factors of these efforts were the best available technology available at a reasonable price. The results of this policy were different from country to country, mainly due to different economic possibilities. The effects of these efforts can very clearly be shown in trend data of pollution levels at long term, as for instance from three different sites in Germany.



*Fig. 5: Time series of annual sulphur dioxide concentrations in Germany from 1961 – 1994. Represented are the industrial sites Gelsenkirchen (West-Germany), Wolfen (East Germany) and the background site Waldhof.*

The gain of knowledge in respect of the weathering processes and the availability of quantitative data as dose-response functions, namely those evaluated within the material exposure programme of the UN ECE (<http://www.corr-institute.se/ICP-Materials/>), which connect corrosion rates and environmental parameters, made it possible to analyse the effects of environment on different targets more precisely than ever before.

It was possible to apply these dose-response functions in a regionally differentiated way at a relative fine scale within the territory of Germany. Corrosion maps obtained in this way show regions of elevated corrosion rates.



*Fig. 6: Map of the annual corrosion rate of bronze in Germany in the years 1993-95 based on dose-response functions from the UN ECE Material Exposure Programme*

The models applied within this mapping procedure allow furthermore calculation of the economic losses due to pollution and to depict them in maps.

## Quantifizierte jährliche Schadenskosten an Wohngebäudeaußenflächen in Deutschland (ICP-Gleichungen)

Datenquellen:  
GWZ95, GWZ87, FGWB,  
Institut für Navigation

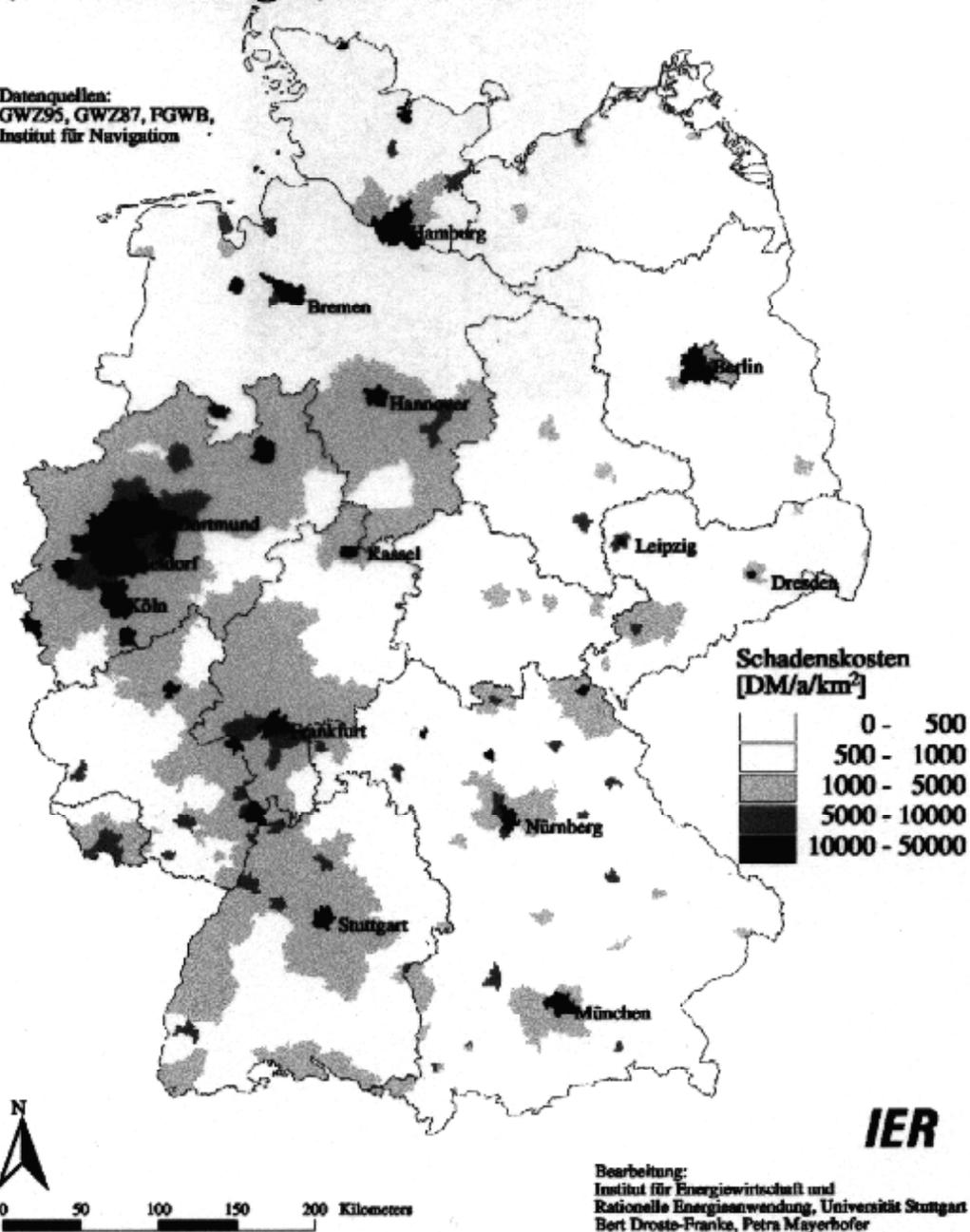


Fig. 7: Quantified annual cost of damage to buildings due to atmospheric corrosion in Germany given as DEM/year/km<sup>2</sup>

Nevertheless, these possibilities still need further research support, because many necessary input data for the applied models, such as the stock-at-risk of the considered materials or structures is not available in sufficient quality up to now.

### 3. Where do we go?

A substantial reduction of sulphur dioxide has taken place almost Europe-wide. Nitrogen oxides and ozone remain to be a problem, especially for those corrosion processes where acid deposition and oxidation play a crucial role.

Many new materials were introduced not only in modern constructing industry but also in conservation of monuments as a reaction and preventive measure on the negative effects of acid air pollutants. They should prolong the lifetime of the structures. But they are also subject of decomposition processes, very often with unknown results for the material. Some of these new materials can become to be sources of environmental risk themselves.

One example: stone consolidants based on organic resins contain additives of tin-organic compounds as catalysts. However, some of these compounds (tributyle-tin-organic compound) are toxic. Those treated stone surfaces are still weathering, even when this process may slow down as they release these toxic substances into the environment.

Better and improved knowledge of the mechanisms of corrosion and the formulation quantitative relations between the effects and the parameters (dose-response functions) contributes also to a more detailed understanding of many of the reactions that are "hidden" behind the dominant effect of sulphur dioxide. As an example: some efforts should be directed towards effects of VOCs. They do change the surface wettability of materials and have therefore indirectly influence on the corrosion. They also act as nutrients for microbiological growth and force in this way indirectly corrosion.

In contrary to the repair mechanisms known from biological systems a fundamental property of materials is the irreversibility of macroscopic corrosion processes. It is therefore not possible to find critical loads or threshold levels of air pollutants, below them no damage occurs. Definition of values that are tolerable in respect to "natural" background and to expected life time of monuments have to be discussed and defined, considering social, economic and political reality.

The deterioration of monuments is not a national problem, it does not stop at national borders. An international coordination of research, which is still necessary, should be promoted. The aims should be also directed to an intensive exchange of already available knowledge, this would substantially contribute to an efficient use of existing knowledge-base and make the limited resources available for research and work directed towards problems that still need solutions. Preservation of monuments is a substantial need of the society, it secures the identity of its citizens and is a main economic factor.

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