

Determination of wet and dry deposition of atmospheric pollutants on building stones by field exposure experiments

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Abstract

A field exposure programme at two sites in Germany was carried out. Besides monitoring of ambient pollutant concentrations precipitation samplers were operated. Several types of stone materials and a polycarbonate test specimen as a reference were equipped with run-off water collectors. Results obtained from chemical analysis of precipitation and run-off water are discussed with respect to the role of driving rain as a source or sink for pollutant accumulation in the porous system of the stone materials. For that purpose fluxes of wet and dry deposition as the input were compared to the removal of material from the stone surfaces with running water. The results obtained revealed large differences between the two sites. It was found that the mode of action of driving rain is very complicated. Effects cannot be generalized and are strongly depending on other parameters such as rainfall characteristics (rates, pollutant concentrations), ambient pollution (gases and particulate matter) and the properties of the stone material (especially water uptake behaviour).

Keywords

Run-off water, wet deposition, dry deposition, gypsum, salt enrichment.

Introduction

Both wet and dry deposition can be important to the atmospheric deterioration of building stones. Dry deposition of gases and particles as a continuous process will inevitably lead to the enrichment of soluble and insoluble material at the surface or in the pore system of building stones. Material deposited from the atmosphere may remain unchanged and simply accumulate over long periods of time or it may be subject to subsequent

chemical reactions with the stone material itself or with other compounds deposited from the atmosphere.

In the first case damage or aesthetical impacts may result from soiling, the formation of crusts or surface layers and mainly from the enrichment of soluble salts in the pore space of the stone material. The second process is of utmost importance with respect to carbonate stone (e.g. marble, limestone or carbonate cemented sandstone) because atmospheric strong acids (sulfuric acid, H_2SO_4 , and nitric acid, HNO_3) or their precursors (sulfur dioxide, SO_2 , and nitrogen oxides, NO_x) will react with the carbonate minerals of the stone material (calcite, dolomite) resulting in the formation of the much better soluble sulfates and nitrates.

Wet deposition generally includes all forms of precipitation, but normally rainfall can be regarded as the dominant pathway for the wet deposition of pollutants. Compared to dry deposition the mode of action of rainfall on porous materials is more complicated. The acidity of rainfall may lead to direct attack on mineral compounds of a stone material. Indirect effects include dissolution and transport of previously deposited material and the corrosion products of dry deposition. To study the complex interaction of wet and dry deposition, chemical transformations and subsequent transport processes, chemical analysis of run-off water has proved to be very useful, both, at monuments (e.g. Rönicke and Rönicke 1972, Butlin et al. 1985, Roekkens and Van Grieken 1989) and in field exposure experiments (e.g. Reddy 1990, Cooper et al. 1992, Steiger et al. 1993a). In most of these studies the weathering of carbonate stone by acid deposition has been investigated.

For that purpose the concentration differences between run-off water samples from stone materials and an inert reference surface, termed as the excess concentrations, have been evaluated. Run-off experiments on carbonate stone show large excess concentrations of calcium (Ca^{2+}), Hydrogencarbonate (HCO_3^-) and sulfate (SO_4^{2-}), reflecting the dissolution of calcite (CaCO_3) by the acidity of rain water and the deposition of SO_2 from the

atmosphere. Several authors have used run-off measurements from carbonate stone to determine loss rates of calcite.

Steiger et al. (1993a) have recently published results from run-off experiments with carbonate and silicate stones. They found large excess concentrations of calcium and sulfate in run-off water from Obernkirchen sandstone, a practically pure silicate sandstone, and also high gypsum accumulations of about 0.4 wt% in surface samples from the same stone material after an exposure time of only three years. They concluded that there must also be a significant contribution of atmospheric calcium deposition. In addition to these results it is the objective of this paper to provide an evaluation of the different fluxes determining the accumulation of gypsum and other compounds in the test specimens at our field exposure sites.

Experimental setup

A total of 13 different stone materials were exposed at two sites in Germany. The field exposure sites were selected to be representative of different ambient conditions with respect to climate and pollution. One site (Holzkirchen, Bavaria, approx. 60 km south of Munich) is characterized by moderate to low pollutant concentrations. The other site (Duisburg, Ruhr area) is located in a highly industrialized urban area.

The test specimens (base: 20 x 30 cm²; height: 45 cm) were equipped with run-off water collectors at each of the vertical surfaces. In addition, a polycarbonate test body of the same geometry was also used to collect run-off water (called reference in the following). Surface samples of the test specimens were taken at the begin-

ning of the programme to determine the background level and afterwards once a year from each of the vertical surfaces.

Concentrations of the inorganic cations (calcium, magnesium, sodium, potassium, ammonium and the hydrogen ion) and anions (sulfate, nitrate, chloride and carbonate species) were determined in the precipitation and run-off samples and the surface samples from the test specimens as well. Further details about sampling and analysis procedures can be found in Steiger et al. (1993a).

Ambient concentrations of SO₂, NO_x and total suspended particulate matter were continuously monitored at both exposure sites. Other compounds were analysed during summer and winter measuring campaigns at each site (see Stoffregen 1991 for details of the monitoring programme).

Transport processes

If rainfall hits the surface of a porous material it first will be absorbed by capillary transport (infiltration). In the case of natural stone and many other porous building materials it was found empirically that the cumulative infiltration I is proportional to the square root of time if water is freely available at the surface. It follows that the rate of infiltration $i(t)$ is proportional to $t^{-1/2}$, as is schematically shown in fig. 1. If the source of liquid water is rainfall however, the initial maximum rate of water uptake q_0 is given by the rate of driving rain $R(t)$ onto the vertical surface of a stone facade. When the rate of driving rain exceeds $i(t)$ the stone material becomes saturated and the excess water will start to run off. The process of infiltration is now controlled by the infiltrability of the stone $i(t)$.

Thus the effects of driving rain can be characterized by two phases of a rainfall event. During the first phase (no run-off) rainfall is a source of pollutants which are transported into the interior. In addition soluble compounds which have been previously deposited can also be transported into the interior. That fraction (m_{wc}) of the total wet deposition of a dissolved species at time t that remains in the stone due to capillary sorption is then given as the product of the cumulative infiltration I (area below the solid line in fig. 1) multiplied by the concentration c_w of the species in the rain water (it is assumed for simplicity that c_w is constant with time).

$$m_{wc} = c_w \cdot I = c_w \cdot \int_0^t i(t) \cdot dt \quad (1)$$

Thus m_{wc} can be regarded as the net input by driving rain. The indices w and c refer to wet deposition and capillary water uptake.

In the beginning of the second phase the infiltration rate begins to drop and is approaching zero, whereas the

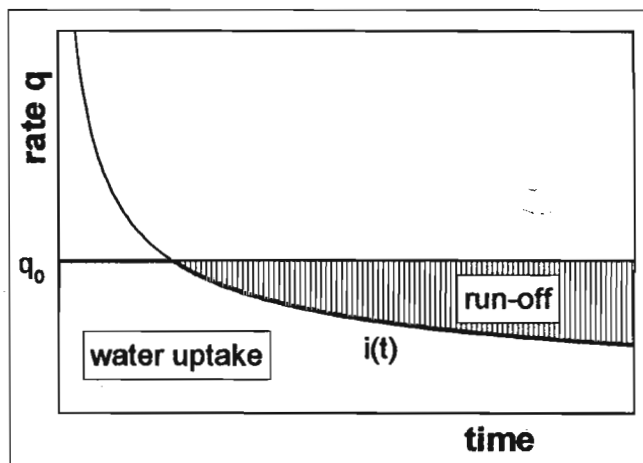


Fig. 1 - Influence of intensity of driving rain on capillary water uptake and the formation of run-off water (see text for further explanation)

amount of running water is increasing with time (hatched area in fig. 1). Again soluble material accumulated at the surface can be dissolved and removed by the run-off water. Due to this cleansing effect rainfall during the second phase may be regarded as a sink with respect to pollutant accumulation.

That fraction of the total wet deposition onto the vertical surface that does not remain in the stone but is transported away with running water (m_{wr}) can therefore be expressed in a similar manner like equation (1) if $i(t)$ is replaced by an appropriate expression for the rate of running water. Thus, the total input of a species onto a vertical surface by wet deposition can be expressed as the sum:

$$m_w = m_{wc} + m_{wr} \quad (2)$$

If it is assumed that m_w is identical for all vertical surfaces of the same exposure, it can be determined for each test specimen from the run-off measurements of the reference.

$$m_w = v_{pc} \cdot c_w \quad (3)$$

v_{pc} is the run-off volume obtained from the reference and c_w is the concentration in the incident rainfall. An expression similar to (2) can also be obtained for the dry deposition of aerosol particles subject to subsequent dissolution and transport processes with rain water.

$$m_d = m_{dc} + m_{dr} \quad (4)$$

The index d refers to dry deposition of particles and c and r again refer to capillary uptake and run-off, respectively. If it is further assumed that dry deposition of aerosol particles is also identical for all vertical surfaces (same direction of exposure). Thus the total input of dry particle deposition for a given period of time can also be determined from the reference.

$$m_d = v_{pc} \cdot (c_{r,pc} - c_w) \quad (5)$$

$c_{r,pc}$ is the concentration in the run-off water from the polycarbonate reference. Thus, the concentration difference in (5) is the excess concentration in the run-off water from the reference surface. It is, however, assumed now that there is no contribution of gas phase deposition onto the inert surface of the reference (see discussion below). The total input of driving rain and dry deposition of particles is then given by:

$$m_w + m_d = m_{r,pc} = v_{pc} \cdot c_{r,pc} \quad (6)$$

In most run-off water studies $c_{r,pc}$ is used to calculate excess concentrations from the stone run-off concentra-

tions. Usually from these excess concentrations stone recession rates for carbonate stone are calculated. However, the use of concentrations instead of fluxes is only correct, if the capillary water uptake of the stone material can be neglected ($m_c = 0$). This will be a good approximation only for very dense stones like marbles as has been shown by Reddy (1990) for the marble used in the NAPAP program. In our experiments, however, the capillary water uptake could not be neglected. Thus fluxes instead of concentrations had to be used.

Once the total input from the atmosphere on the vertical surfaces of the test specimens is known it can be compared to the output by running water, which is given by:

$$m_{rj} = v_j \cdot c_{rj} \quad (7)$$

Here j refers to the stone materials. The net input of a species is then given by:

$$m_j = m_w + m_d - m_{rj} \quad (8)$$

Thus, if the total input of a species exceeds the output by running water ($m_j > 0$), wet deposition and dry deposition of particulate matter result in an enrichment of that species in the stone material. In the case of sulfate, nitrate, chloride and ammonium additional enrichment due to dry deposition of gaseous species has to be considered. If the output exceeds the input ($m_j < 0$) there is a mobilization of compounds. On the one hand this could be due to removal of accumulations from gas phase deposition, on the other hand, negative m_j 's for calcium, magnesium, sodium and potassium must be attributed to the mobilization of these elements from mineral phases of the stone material. By measurement of the different species in the stone material the balance may be completed and the net enrichment or depletion can be determined.

Results and discussion

For a period of one year we have complete precipitation and run-off data from the stone test specimens and the reference at both test sites. From these data the cumulative total input by wet and dry deposition has been calculated as described before. The results are presented in fig. 2. As can be easily seen the total input of the elements calcium, magnesium, potassium and sodium is roughly an order of magnitude higher in Duisburg than in Holzkirchen. These findings are in good agreement, both, with the concentrations of these elements in the atmosphere and the precipitation as well, which are given in table I. Dry deposition of particulate matter is the dominant pathway for the total input of calcium, magnesium and potassium in Duisburg, whereas

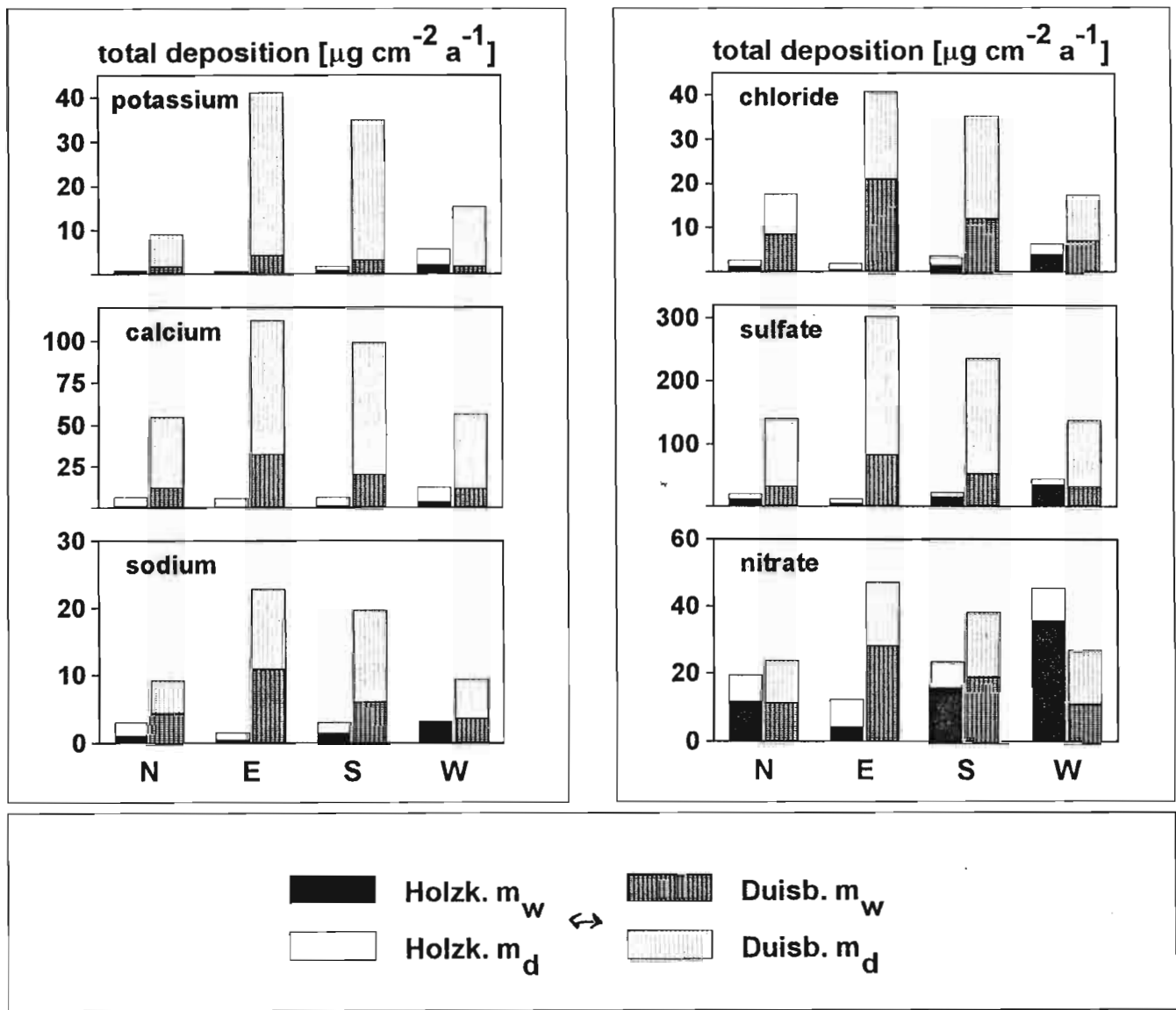


Fig. 2 - Total input by driving rain and dry deposition of particulate matter on vertical surfaces of different exposure in Holzkirchen and Duisburg.

for sodium wet and dry deposition are comparable. In Holzkirchen the influence of dry deposition is less pronounced, only the calcium input is clearly dominated by particle deposition.

In the case of nitrate the differences between the two sites are much less pronounced as could be expected from a comparison of the nitrate concentrations in table I. However, a significant contribution of gaseous nitric acid to the nitrate concentrations in the run-off water from the reference cannot be ruled out, since nearly any surface can be regarded as an ideal sink für HNO_3 . It is difficult, however, to estimate the degree of error in the

dry deposition data for nitrate. But obviously wet deposition becomes much more important in comparison to the elements mentioned before.

Similar deposition patterns were also obtained for ammonium at the two sites. However, because there may be a contribution of the deposition of gaseous ammonia (NH_3), we expect similar uncertainties as for nitrate.

Dry deposition from the gas phase may also affect the sulfate concentrations in the run-off from the reference. Though we would not expect polycarbonate to be a good absorber for SO_2 it has to be pointed out, that the deposition of alkaline particles (e.g. calcite) might build

	Holzkirchen		Duisburg	
	rain [mg/l]	aerosol [$\mu\text{g}/\text{m}^3$]	rain [mg/l]	aerosol [$\mu\text{g}/\text{m}^3$]
Na	0,21	0,28	1,5	2,10
K	0,08	0,19	1,21	1,02
Ca	0,15	0,50	4,34	4,41
Mg	0,04	0,14	0,82	0,92
NH ⁴⁺	0,82	1,6	2,34	4,1
HCO ³⁻	<0,2	-	3,36	-
Cl ⁻	0,25	0,25	3,20	3,8
SO ₄ ²⁻	1,98	3,5	12,8	12,7
NO ₃ ⁻	2,08	3,7*	4,53	8,2*
pH	4,6	-	5,1	-

* total inorganic nitrate

Table 1 - Average ambient concentrations of particulate matter and volume weighted average concentrations in precipitation at the two test sites.

up an alkaline surface layer on the reference, which would be much more favourable for the deposition of SO₂. Indeed we found large excess concentrations of HCO₃⁻ in the run-off water from the reference surfaces, so that excess sulfate measurements are probably also affected by dry deposition of SO₂ to a certain extent.

The results for the chloride deposition are very similar to that obtained for sodium. The total input is much higher in Duisburg than in Holzkirchen. At both sites about half of the total input is from wet and dry depositions respectively. The question arises if there is also a contribution of gas phase dry deposition of hydrochloric acid (HCl). The correlation between sodium and chloride in the run-off samples from the reference are very large however, indicating that dry deposition of sodium chloride is the main source for the excess concentrations of the two ions in the run-off from the reference. Finally it can be seen that both, wet and dry deposition are depending on the direction of exposure at both sites, which for the wet deposition is simply given by the amount of driving rain on the different surfaces. Therefore wind direction and wind speed during a rain event are the dominant parameters, which are also strongly influencing dry deposition of particulate matter.

We then compared the total input for the different species to the output according to equation (8). As mentioned before $m_i > 0$ implies a net enrichment in a test specimen by wet and dry particle deposition. For example at both test sites the atmosphere is a source of chloride for all stone materials of either direction of exposure. Therefore chloride accumulates in the porous system of the stone materials. According to the results from fig. 2 the

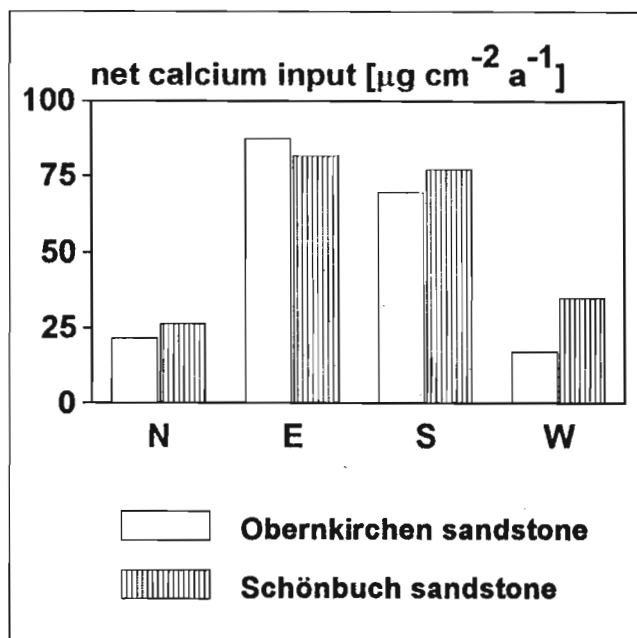


Fig. 3 - Net input of calcium on the vertical surfaces of Obernkirchen sandstone and Schönbuch sandstone in Duisburg

net enrichment is of course much higher in Duisburg than in Holzkirchen. In addition to chloride we also found positive m_i 's in Duisburg for potassium, sodium, ammonium and with few exceptions calcium and magnesium.

The results of the calcium balance for Obernkirchen sandstone (lower cretaceous) and Schönbuch sandstone (upper triassic) are presented in fig. 3. In both stone materials only traces of carbonate minerals are present. It has to be concluded that at least some fraction of the gypsum accumulation found in surface samples from these stones can be attributed to deposition of calcium preferably either as sulfate or as carbonate, which would subsequently be attacked by the deposition of SO₂. The atmosphere in Duisburg proved to be a net calcium source for all of the east and north exposed surfaces (including the carbonate stones) and all but one (a very dense limestone with small water uptake) of the south exposed surfaces. This is not to say that there is no dissolution of carbonate minerals by acid deposition. It simply means that neither the calcium deposited from the atmosphere nor the reaction product of acid attack on carbonate minerals are effectively removed by running water. Thus, if calcium loss as a measure of stone damage would be simply calculated from excess concentrations in run-off water the results would be erroneous and misleading with respect to the principal mechanism of damage.

The results in Holzkirchen markedly differed from that

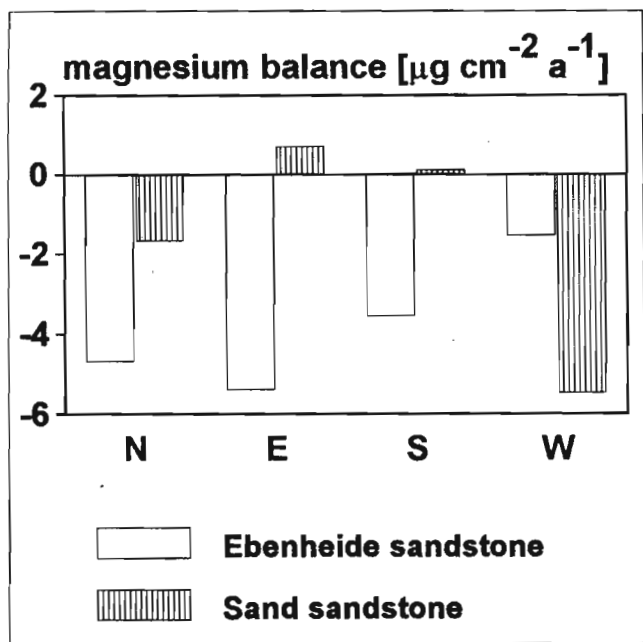


Fig. 4 - Magnesium balance for Ebenheide sandstone and Sand sandstone in Holzkirchen

in Duisburg. The removal of calcium from the carbonate test specimens was much more efficient than in Duisburg. Balancing the calcium concentration in the net run-off versus sulfate and bicarbonate revealed that most of the calcium loss is due to the acidity of rainfall (Steiger et al. 1993a). A net depletion was also observed for other elements in Holzkirchen. As an example fig. 4 shows the results for the magnesium balance of Ebenheide sandstone (lower triassic) and Sand sandstone (upper triassic). For nearly all directions of exposure m_i was found to be negative, thus indicating magnesium loss from the stones. Since both stone materials contain chlorite (Grimm 1990) it can be assumed that magnesium is mobilized from that mineral by the attack of acid deposition. In Holzkirchen we also observed depletion of potassium and sodium from stones containing other clay minerals and feldspars further confirming the dissolution of minerals other than carbonates.

It should be possible to detect the net enrichment of compounds predicted from the evaluation of the run-off data in the surface samples from the test specimens. However, as mentioned before the enrichment will not necessarily be observed near the surface. Zones of accumulation may also be found in greater depths due to capillary transport, as it has been observed at several German monuments (Steiger et al. 1993b). It is therefore necessary to measure profiles from drillcores to accurately determine the enrichment of water soluble species. To preserve the surfaces of the test specimens for further

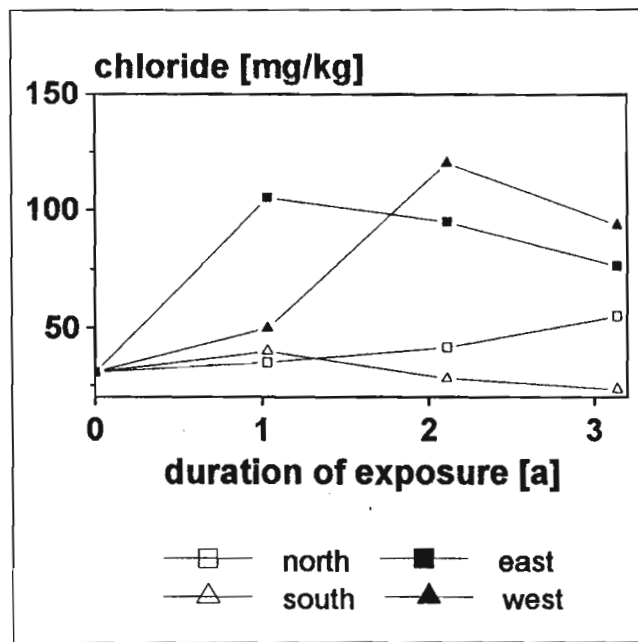


Fig. 5 - Chloride concentrations in surface samples from Eichenbühl sandstone in Duisburg

run-off experiments, we did not yet take drillcores. Therefore the results from the surface samples can only be regarded as preliminary. The strong enrichment of gypsum in the Duisburg stones has been already published in Steiger et al. (1993a). As a further example fig. 5 shows results of chloride enrichment in surface samples from Eichenbühl sandstone (lower triassic). Though there is not such a clear trend as it was found for gypsum the results confirm the accumulation of chloride in the test specimens.

Conclusions

The study shows that in run-off experiments fluxes instead of excess concentrations in the run-off water have to be used, to accurately determine the net amount of a species that is removed from a stone surface. Otherwise erroneous and misleading results may be obtained.

It was further shown that there may well be a significant contribution of the deposition of calcium rich particles from the atmosphere to large gypsum accumulations in sandstones. This is an important finding with respect to the formation of gypsum crusts on silicate sandstone which is often observed at German monuments (Neumann et al. 1993). In addition to calcium also other species, e.g. sodium chloride, may accumulate in the porous system of stone materials as a result of driving rain and dry deposition of particulate matter. This could be of rel-

evance in coastal regions where enhanced concentrations of sea salt are found both in rain water and in suspended particulate matter.

The results from Holzkirchen show, that, if reactive carbonate minerals are not present in the stone material and if there is no significant input of such minerals from the atmosphere, acid deposition will also dissolve other minerals like clays and feldspars.

It can be concluded that the role of driving rain in the weathering of building stones is very complex. It strongly depends on the interaction of many different parameters. Among others, the chemical composition of precipitation, the ambient concentrations of gaseous and particulate pollutants, the properties of the stone material with respect to water uptake and the kind of exposure with respect to the input of driving rain and dry deposition have to be taken into account.

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