

DAMAGE FUNCTIONS AND MECHANISM EQUATIONS DERIVED FROM LIMESTONE WEATHERING IN FIELD EXPOSURE

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(Received 9 May 2000; accepted 29 October 2001)

Abstract. In this article damage functions and mechanism equations are elaborated for Massangis limestone, exposed to ambient atmospheric conditions. Limestone slabs were placed in five different environments in Belgium and run-off water was collected for chemical analyses, over a 3 yr period. To elucidate the weathering mechanism and the relative contributions of different deleterious factors, calcium concentrations in run-off water were regressed versus the total (wet + dry) deposition of ions onto the stone, gaseous atmospheric pollutant concentrations and meteorological parameters. The data matrix (30 000 analytical results) was interpreted using Multiple Linear Regression (MLR) and Partial Least Squares Regression (PLS). Mechanism equations and damage functions were first established for each of the five studied sites separately and subsequently pooled regressions were calculated. A damage function is proposed and compared with limestone damage functions found in the literature, after introducing the field data presented in this work into the respective functions. Massangis limestone mass loss is best predicted with a PLS model. Rainwater volume is the most decisive factor in causing mass loss at all sites, and sulphate and bicarbonate are the most important weathering products. Models established using MLR result in less reliable predictions of mass loss compared to PLS.

Keywords: damage functions, environmental studies, field studies, Massangis limestone, mechanism equations, multiple regression methods, stone decay

1. Introduction

Mechanism equations are calculated to elucidate the stone weathering mechanism by studying the relative contributions of ionic species released from the surface and dissolved in the run-off water. Damage functions are computed to predict material decay as a function of environmental conditions, and to assess the relative contribution of each of the deleterious factors (Benarie, 1991; Livingston, 1997). In order to be useful, credible and widely applicable damage functions should be consistent with the underlying theory, statistically robust and easy to verify under realistic ambient conditions. They must account for all the forces that may influence the rate of degradation, e.g. air pollutants, deposited dust, various forms of atmospheric moisture (rain, relative humidity, etc.), and thermal variations (temperature, freeze-thaw cycles, etc.). Material weathering rates can be measured by monitoring the chemistry of run-off water, mass loss and surface recession



Water, Air, and Soil Pollution **139**: 75–94, 2002.

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(Webb *et al.*, 1992). Material loss from stones occurs by two major routes: physical factors (e.g. abrasion, erosion, flaking, etc.) and chemical dissolution as a result of the interaction with rainwater (Webb *et al.*, 1992). Exposing stones to realistic dry and wet deposition, and collecting run-off water for laboratory analyses, in a precisely defined area at frequent intervals, provides reliable information about stone weathering (Cooper, 1985). The aim is to quantify the material behaviour under ambient atmospheric conditions, since test chambers can not replicate all atmospheric conditions (Lipfert, 1989a; Butlin *et al.*, 1992; O'Brien *et al.*, 1995). It should however be noted that differences in the approach to measure weathering rates and including different environmental parameters into the mass loss prediction model can produce results that are not directly comparable.

Many damage functions for different materials have been proposed in the literature. Benarie and Lipfert (1986) and Reisener *et al.* (1995) proposed functions to describe metal corrosion, Kucera and Fitz (1995) and Yerrapragada *et al.* (1996) established functions to predict mass loss from marble and limestone, and Lipfert (1989a) gave an overview of damage functions for precipitation based loss rates for calcareous stones. The UN/ECE have commissioned major studies on building stone weathering, including damage functions for limestone (e.g. Ashall *et al.*, 1998; Tidblad *et al.*, 1998). These functions include only a few of the potentially deleterious factors that control stone decay, but when combining variables from exposure studies enormous data sets result and more advanced statistical data processing becomes necessary. Normally Multiple Linear Regression (MLR) is applied, however, this method is not the most suitable when the data set contains collinear variables, which is often the case for environmental data. Therefore, besides MLR, another statistical approach, namely Partial Least Squares (PLS) regression, has been applied in this work. PLS offers the possibility to combine collinear variables in the *X*-matrix and to decide which variables contribute to explain the variance with the *Y*-matrix (= limestone mass loss). Although the results are simple statistical relationships, realistic estimations of decay rates are guaranteed since data from exposure to ambient conditions were used. Finally, the data collected in this study were introduced into different limestone damage functions for limestones found in the literature, in order to evaluate the accuracy of the damage function proposed in this work.

2. Sampling and Analytical Techniques

Massangis limestone slabs (calcite content > 98% with a, mainly intergranular, porosity of 8–13%) were exposed in micro-catchment units (mcu) to collect rainwater that has run over the stones, better known as 'run-off water' (Jeffrey *et al.*, 1985). The slabs, measuring 25 × 25 × 5 cm were placed in a glass holder, cemented on top of a polystyrene box and oriented towards the prevailing driving rain direction (SW), with an inclination angle of 15°. The polystyrene box was filled

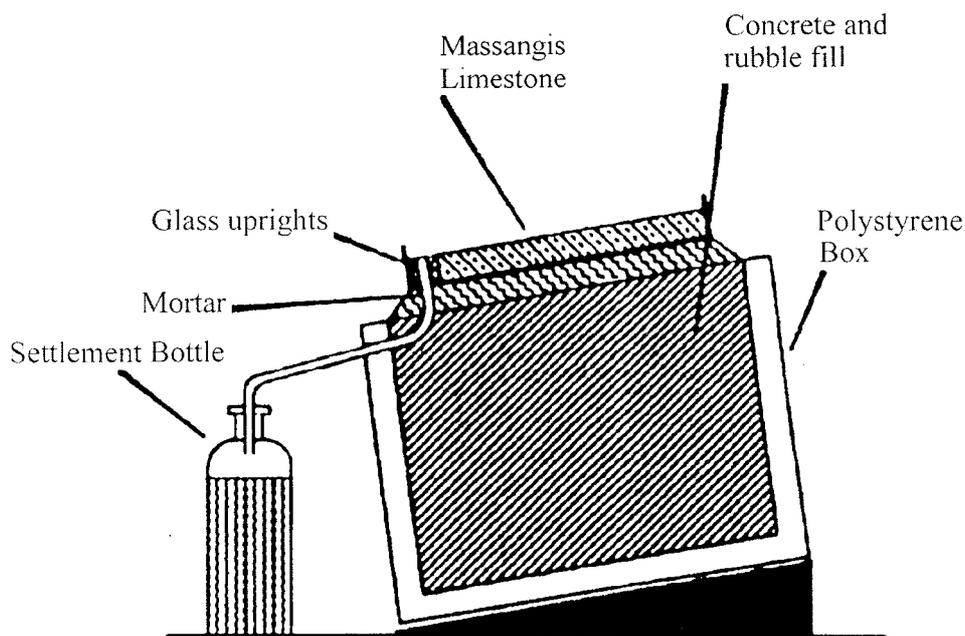


Figure 1. Schematic representation of a micro-catchment unit (mcu).

with gravel in order to normalise as much as possible differences in the temperature of the limestone slab. The run-off water was collected in PE bottles (Figure 1). During three years (1988–1991) run-off water was sampled weekly at five sites in Belgium (Vleugels, 1992): On top of the chemistry department building of the University of Antwerp located in a suburban area (UIA), in a street with heavy traffic in the centre of Antwerp (PML), in the polluted port area of Antwerp next to major oil refineries (PORT), at the Belgian seaside (SEA), and at rural site located on a hillside in the Ardennes in southern Belgium (OFF). At each site, two stone slabs were exposed together with two roughened glass plates of the same dimensions serving as blanks. The ‘Institute for Hygiene and Epidemiology’ (IHE, 1988–1992) in Belgium supplied data on the concentrations of gaseous atmospheric pollutants (SO_2 , NO, NO_2 , C_nH_m , O_3) and deposition of dust. Meteorological parameters (temperature = T, relative humidity = RH, rainfall amount = mmR, rain intensity = RI, wind speed and direction = WS, number of freeze-thaw cycles = FT, and number of days with snow = SN, storm = ST and hail = Ha) were obtained from the ‘Royal Meteorological Institute’ (KMI, 1988–1992). The average environmental conditions of the exposure sites are described in Table I. During this field exposure experiment, around 1500 run-off water samples and 1500 blanks were collected. A data set containing more than 30 000 analytical results from run-off water and blank samples, together with more than 5000 meteorological and atmospheric pollutant measurements was obtained (Vleugels, 1992).

TABLE I
Average environmental conditions at the exposure sites in Belgium

Site	SO ₂ ($\mu\text{g m}^{-3}$)	NO ₂ ($\mu\text{g m}^{-3}$)	T (°C)	Rain (mm yr ⁻¹)	pH _{rain}
UIA	29	30	10	700	3.6
PML	27	55	11	650	3.7
PORT	59	49	12	750	3.7
SEA	9	20	10	650	4.4
OFF	12	12	7	950	4.5

The volume of the run-off water was determined, and subsequently filtered over a cellulose filter (Whatman 41), which was weighed before and after filtration to determine total suspended particulate matter (TSP). NH₄⁺ and pH were determined potentiometrically as soon as possible. HCO₃⁻ was measured by acidimetric titration using HCl on a methyl orange indicator. Concentrations of the anions (NO₂⁻, NO₃⁻, Cl⁻ and SO₄²⁻) were determined with Ion Chromatography (IC) using a Dionex 4000i instrument equipped with an AS4A separator column. Concentrations of cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) were analysed by Atomic Absorption and Atomic Emission Spectrometry (Perkin Elmer 3030 spectrometer).

3. Results and Discussion

When rainwater impacts onto a stone and flows over its surface, ions are exchanged between rainwater and stone. Since the amount of calcium contained in run-off water is a measure of the dissolution and removal of calcium carbonate from the limestone surface, the dissolved net calcium in run-off water can be used to determine the stone surface recession (Sherwood and Reddy, 1988). *Mechanism equations* were computed by regressing net calcium concentration in the run-off water (Ca_{RO}²⁺) from limestone versus the net concentrations of the other ions dissolved in the run-off water (X_{RO}^{Y±}). Net ion concentrations resulting from the interaction of rainwater with the limestone surface were obtained by subtracting the blank concentrations from the run-off water concentrations, following the same approach as Reddy and Werner (1985). Results were expressed in $\mu\text{eq m}^{-1}$ per week, i.e. 625 cm² per week.

Damage functions were calculated by regressing the net calcium concentration in the run-off water (Ca_{RO}²⁺) versus the blank total deposition ion concentrations (X_{TD}^{Y±}), the meteorological parameters and the atmospheric pollutant data. The factors determining mass loss were identified as follows: First, mechanism equations and damage functions were regressed for the five sites separately. Next,

TABLE II

MRL statistics for *mechanism equations* of the Massangis limestone exposed in Belgium. Ca^{2+} loss in $\mu\text{eq}/\text{m}^2/\text{week}$. R^2 = correlation coefficient, M = measured Ca^{2+} loss, P = predicted Ca^{2+} loss

Site	$\text{Ca}_{\text{RO}}^{2+} = a_0 + a_1 \text{SO}_{4\text{RO}}^{2-} + a_2 \text{HCO}_{3\text{RO}}^{-}$					
	a_0	a_1	a_2	R^2	M	P
UIA	250**	1.2***	0.9***	0.53	995	1000
PML	230***	1.1***	1.1***	0.74	1040	1040
PORT	470***	1.1***	0.9***	0.69	1700	1720
SEA	540***	2.0***	0.5***	0.41	860	980
OFF	190***	1.0 ^{ns}	1.1***	0.76	890	1000

*: Significant at $\alpha < 0.05$; **: significant at $\alpha < 0.01$; ***: significant at $\alpha < 0.001$.

^{ns}: Not significant at $\alpha > 0.05$.

to determine the mass loss of Massangis limestone in Belgium, a pooled damage function and mechanism equation, including all data, were calculated. Since not all the parameters contribute to the same extent to the damage function, the pooled model was recalculated including only the most relevant variables (*restrained* pooled damage function). The predictability of this model and the damage functions from literature were compared with the data set presented in this article. Two regression methods were applied to calculate the mechanism equations and the damage functions: Multiple Linear Regression (MLR) and Partial Least Squares Regression (PLS). MLR simultaneously uses various variables x_i to predict one or more variables y . The model can be written in the form (Walker and Lev, 1969):

$$y = a_0 + a_1x_1 + a_2x_2 + \dots + a_nx_n .$$

Among other pitfalls, MLR fails if correlations exist between the x -variables. Collinearity of independent variables is often a problem with environmental data, since the atmospheric conditions that cause high concentrations of one pollutant, at a given place or time, may very well increase the concentrations of other pollutants (Lipfert, 1989a), resulting in similar temporal and spatial trends for both pollutants. PLS is not sensitive to collinearity in the X -matrix. PLS calculates components, which efficiently describe the covariance structure in a data matrix (X) and which are predictive for the Y -matrix. PLS is a good alternative to the more generally applied MLR because it is more robust, i.e. adding calibration samples to the matrix will not greatly change the model parameters (Geladi and Kowalski, 1986; Lorber *et al.*, 1987). PLS calculations were performed using the UNSCRAMBLER software package (Tysso *et al.*, 1987).

3.1. MECHANISM EQUATIONS

The relative contribution of SO_4^{2-} and HCO_3^- (the two most abundant anions in the run-off water) to calcium leaching from the stones was determined for the five sites separately. MLR was used since these anions were assumed not to collinear (Table II). Ion amounts are expressed in $\mu\text{eq}/\text{m}^3/\text{week}$. The subscript RO indicates the concentrations in the run-off water. The significant intercepts (a_0) may indicate either involvement of other (not included) important factors or non-linear relationships (Lipfert, 1989a). The regression coefficients of SO_4^{2-} and HCO_3^- (versus Ca^{2+}) are significant at all locations, except at OFF. The predominance of the contribution of HCO_3^- to stone loss in OFF may be due to the higher rainfall amount and the lower ambient temperature, which increases the solubility of CO_2 and enhances calcareous stone dissolution. To evaluate the regression, the calcium losses as predicted from the average SO_4^{2-} and HCO_3^- concentrations in blank run-off water, are compared with the mean measured calcium losses (Table II). Predictions of the calcium loss based on SO_4^{2-} and HCO_3^- agree well with the corresponding predicted values. Limestones at PORT present the highest calcium loss, UIA and PML show similar moderate losses, while at SEA and OFF the lowest losses are observed. The material loss rate increases at sites with higher SO_2 levels, as can be seen from Table I.

PLS allows regressing a dependent variable versus a large series of independent, but collinear variables. After eliminating outlying samples, optimised equations expressing the calcium loss of the limestone as a function of all measured ions contained in the run-off water, were computed (Table III). Ion amounts are expressed in $\mu\text{eq}/\text{m}^3/\text{week}$. The highest correlation was found at OFF. At all sites the correlation coefficients were higher when applying PLS compared to MLR. The intercepts were significant at all sampling sites, and the H_{RO}^+ coefficient was generally negative, although not significant. Since the pH of rainwater rises when flowing over limestone, the H_{RO}^+ is negative but the contribution to the stone loss is positive. Only in the centre of Antwerp (PLM), H_{RO}^+ had a significant coefficient. The coefficient of HCO_3^- was significant at all sites. The Ca^{2+} - SO_4^{2-} correlation was important only for the most polluted areas at PORT, PML and UIA. Cl^- showed an important contribution in the harbour of Antwerp, but unexpectedly not at SEA. This may be due to a prolonged Cl^- uptake caused by Cl^- enriched rainwater in coastal areas (Vleugels, 1992). The generation of HCl from domestic waste incinerators at the most polluted sites might also contribute to this observation, albeit to a small extent. A significant Ca^{2+} - NO_3^- correlation was found at PML and PORT, two sites with heavy traffic.

Table III compares predicted calcium losses with measured calcium losses. PLS results in a better fit, compared to MLR. PLS indicates that HCO_3^- and SO_4^{2-} are by far the most important weathering products, together with calcium loss from the stones. Correlations between calcium and HCO_3^- and SO_4^{2-} , respectively, vary from site to site. Calcium loss was only slightly influenced by the loss of NO_3^-

TABLE III

PLS statistics for the *mechanism equations* of the Massangis limestone exposed in Belgium. Ca^{2+} loss in $\mu\text{eq}/\text{mcu}$ week. R^2 = correlation coefficient, M = measured Ca^{2+} loss, P = predicted Ca^{2+} loss

Sites	$\text{Ca}_{\text{RO}}^{2+} = a_0 + a_1 \text{H}_{\text{RO}}^+ + a_2 \text{Cl}_{\text{RO}}^- + a_3 \text{NO}_{3\text{RO}}^- + a_4 \text{SO}_{4\text{RO}}^{2-} + a_5 \text{HCO}_{3\text{RO}}^- + a_6 \text{Mg}_{\text{RO}}^{2+} + a_7 \text{Na}_{\text{RO}}^+ + a_8 \text{K}_{\text{RO}}^+$											
	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	R^2	M	P
UIA	650***	-0.06 ^{ns}	0.88**	1.1 ^{ns}	0.48**	0.42**	4.6**	0.51 ^{ns}	1.0 ^{ns}	0.80	968	967
PML	580***	-0.28**	1.1**	2.3*	0.54***	0.52***	4.4*	0.62 ^{ns}	0.52 ^{ns}	0.76	1000	1000
PORT	1000***	0.28 ^{ns}	1.2***	1.8**	0.54***	0.55**	1.9 ^{ns}	1.3*	2.4**	0.72	1630	1630
SEA	580***	-0.83 ^{ns}	0.33 ^{ns}	2.6 ^{ns}	0.93*	0.42***	2.0 ^{ns}	0.37 ^{ns}	1.5 ^{ns}	0.79	812	812
OFF	180***	-0.59 ^{ns}	0.46 ^{ns}	0.66 ^{ns}	4.4*	0.52***	22.0 ^{ns}	0.15 ^{ns}	0.3 ^{ns}	0.88	880	881

Symbols: see Table II.

TABLE IV

MLR statistics for the *damage functions* of the Massangis limestone exposed in Belgium. Ca^{2+} loss in $\mu\text{eq}/\text{mcu}$ week. R^2 = correlation coefficient, M = measured Ca^{2+} loss, P = predicted Ca^{2+} loss

Sites	$\text{Ca}_{\text{TD}}^{2+} = a_0 + a_1 \text{H}_{\text{TD}}^+ + a_2 \text{SO}_{4\text{TD}}^{2-} + a_3 \text{HCO}_{3\text{TD}}^- + a_4 \text{NO}_{3\text{TD}}^-$					R^2	M	P
	a_0	a_1	a_2	a_3	a_4			
UIA	790***	0.01 ^{ns}	0.5 ^{ns}	-0.4 ^{ns}	2.0 ^{ns}	0.06	971	932
PML	1200***	-0.02 ^{ns}	-0.5**	-0.8 ^{ns}	0.3 ^{ns}	0.08	1030	1110
PORT	1030***	-0.2 ^{ns}	2.3***	0.9 ^{ns}	-0.3 ^{ns}	0.19	1710	1750
SEA	330*	0.4 ^{ns}	3.2***	-0.6 ^{ns}	0.6 ^{ns}	0.20	859	891
OFF	300***	1.0*	4.6***	2.5***	-3.0*	0.39	879	893

Symbols: see Table II.

and Cl^- . Rain acidity only affected limestone weathering at the centre of Antwerp (PML) on a short time interval of one week.

3.2. DAMAGE FUNCTIONS

The net calcium loss was regressed versus the blank total deposition ion concentrations for each site separately. Table IV shows the intercepts, and the regression and the correlation coefficients of the equations obtained with MLR, when regressing Ca^{2+} versus the total deposition input of H^+ , SO_4^{2-} , HCO_3^- and NO_3^- ($\mu\text{eq}/\text{mcu}/\text{week}$) on the (blank) glass plates. To prevent confusion with the mechanism equations, the subscript TD is added to refer to total deposition input. The correlation coefficients are much lower than those found for the mechanism equations. The intercepts are significant in all sampling sites. The contribution of H^+ and NO_3^- to the stone loss is negligible. The deposition of HCO_3^- and SO_4^{2-} onto the limestone determine the mass loss at OFF. The input of HCO_3^- increases due to the higher rainwater pH and the higher rainfall amount. The total deposition of SO_4^{2-} determines the mass loss at all sites, except at UIA. At this location the regressed equation is not very useful, since none of the variables show a significant contribution to predict the calcium loss.

Experimentally determined calcium loss was compared with predicted calcium loss and the obtained results were poorer than in the case of the mechanism equations. In view of the low correlation coefficients, large intercepts and small significance of the regression coefficients, MLR does not seem to be the best method to calculate the damage functions. These shortcomings were probably caused by collinearity between x -variables. To cope with this problem, PLS was applied. The unweighted regression coefficients permitted to select the variables that were useful in the model (Unscrambler, 1991), since they indicate which x -variables explain

TABLE V
 PLS statistics for the *damage functions* of the Massangis limestone exposed in Belgium. Ca^{2+} loss in $\mu\text{eq}/\text{m}^2/\text{week}$. R^2 = correlation coefficient, M = measured Ca^{2+} loss, P = predicted Ca^{2+} loss

Sites	R^2	M	P
UIA	0.7	959	959
		$\text{Ca}_{\text{RO}}^{2+} = 120^{***} + 0.14 \text{Vol}_{\text{TD}}^* + 0.26 \text{H}_{\text{TD}}^{+ \text{ns}} + 0.3 \text{Cl}_{\text{TD}}^{- \text{ns}} +$ $1.2 \text{NO}_{3\text{TD}}^{- \text{ns}} + 0.47 \text{SO}_{4\text{TD}}^{2+ \text{ns}} + 0.33 \text{Ca}_{\text{TD}}^{2+ \text{ns}} + 1.6 \text{Mg}_{\text{TD}}^{2+ \text{ns}} + 1.0 \text{K}_{\text{TD}}^{+ \text{ns}} - 8.9$ $\text{FT}^{\text{ns}} + 6.5 \text{mmR}^* + 17 \text{WS}^{\text{ns}} + 76 \text{SN}^{\text{ns}} + 48 \text{HA}^{\text{ns}} + 56 \text{ST}^{\text{ns}}$	
PML	0.8	925	924
		$\text{Ca}_{\text{RO}}^{2+} = 350^{***} + 0.14 \text{Vol}_{\text{TD}}^* + 2.0 \text{TSP}_{\text{TD}}^* + 0.39 \text{Cl}_{\text{TD}}^{- **} + 0.43 \text{SO}_{4\text{TD}}^{2- *}$ $+ 0.43 \text{HCO}_{3\text{TD}}^{- \text{ns}} + 2.2 \text{Mg}_{\text{TD}}^{2+ ***} + 0.41 \text{Na}_{\text{TD}}^{+ **} + 0.40 \text{C}_r \text{H}_r^* - 4.7 \text{T}^{\text{ns}} + 3.6 \text{RH}^{**} + 5.7$ $\text{mmR}^{***} + 28 \text{WS}^{***} + 73 \text{SN}^{***} + 74 \text{HA}^{**} + 48 \text{ST}^*$	
PORT	0.8	1650	1650
		$\text{Ca}_{\text{RO}}^{2+} = 760^{***} + 0.23 \text{Vol}_{\text{TD}}^{***} + 0.20 \text{H}_{\text{TD}}^{+ \text{ns}} + 4.0 \text{TSP}_{\text{TD}}^{\text{ns}} +$ $0.23 \text{Cl}_{\text{TD}}^{- \text{ns}} + 0.08 \text{NO}_{3\text{TD}}^{- \text{ns}} + 0.43 \text{SO}_{4\text{TD}}^{2- **} + 0.37 \text{Ca}_{\text{TD}}^{2+ \text{ns}} +$ $2.1 \text{Mg}_{\text{TD}}^{2+ *}$ $+ 0.46 \text{Na}_{\text{TD}}^{+ \text{ns}} + 1.5 \text{K}_{\text{TD}}^{+ \text{ns}} - 6.6 \text{T}^{\text{ns}} - 20 \text{FT}^{\text{ns}} + 7.0 \text{mmR}^{**}$	
SEA	0.7	787	787
		$\text{Ca}_{\text{RO}}^{2+} = 440^{***} + 0.1 \text{Vol}_{\text{TD}}^* + 0.2 \text{TSP}_{\text{TD}}^{\text{ns}} + 0.009 \text{Cl}_{\text{TD}}^{- \text{ns}} + 0.47 \text{NO}_{3\text{TD}}^{- \text{ns}} + 0.55$ $\text{SO}_{4\text{TD}}^{2- *}$ $+ 0.16 \text{HCO}_{3\text{TD}}^{- \text{ns}} + 0.19 \text{Ca}_{\text{TD}}^{2+ \text{ns}} + 0.50 \text{Mg}_{\text{TD}}^{2+ \text{ns}} + 0.11 \text{Na}_{\text{TD}}^{+ *}$ $+ 1.0$ $\text{K}_{\text{TD}}^{+ \text{ns}} - 2.0 \text{NO}_2^{\text{ns}} - 2.7 \text{T}^{\text{ns}} + 8.0 \text{FT}^{\text{ns}} + 7.4 \text{RH}^{**} + 3.8 \text{mmR}^* + 4.9 \text{WS}^{\text{ns}} + 93 \text{HA}^{\text{ns}}$	
OFF	0.9	838	839
		$\text{Ca}_{\text{RO}}^{2+} = -220^{***} + 0.15 \text{Vol}_{\text{TD}}^* + 3.0 \text{TSP}_{\text{TD}}^{\text{ns}} + 0.50 \text{Cl}_{\text{TD}}^{- \text{ns}} + 1.2 \text{NO}_{3\text{TD}}^{- \text{ns}} + 1.5$ $\text{SO}_{4\text{TD}}^{2- \text{ns}} + 0.70 \text{HCO}_{3\text{TD}}^{- \text{ns}} + 0.51 \text{Ca}_{\text{TD}}^{2+ \text{ns}} + 3.3 \text{Mg}_{\text{TD}}^{2+ \text{ns}} + 0.67 \text{Na}_{\text{TD}}^{+ \text{ns}} + 8.9$ $\text{SO}_2^{\text{ns}} - 14 \text{NO}^{\text{ns}} - 5.4 \text{NO}_2^{\text{ns}} - 1.2 \text{O}_3^{\text{ns}} - 6.1 \text{T}^{\text{ns}} + 16 \text{FT}^{\text{ns}} + 2.0 \text{RH}^{\text{ns}} + 2.5 \text{mmR}^{\text{ns}} +$ $19 \text{WS}^* + 33 \text{SN}^{\text{ns}} + 64 \text{HA}^{\text{ns}} - 45 \text{ST}^{\text{ns}}$	

Symbols: see Table II.

the variance within the Y -matrix. The unweighted regression coefficients for the variables are shown in Figure 2. The parameters used for the damage functions were: ion concentrations ($\mu\text{eq}/\text{mcu}/\text{week}$), blank run-off volume ($\text{mL}/\text{mcu}/\text{week}$), TSP ($\text{mg}/\text{mcu}/\text{week}$), atmospheric pollution concentrations of SO_2 , NO , NO_2 , O_3 , C_nH_m and dust ($\mu\text{g}/\text{m}^{-3}$), temperature (T) in $^\circ\text{C}$, the number of freeze-thaw cycles during the sampling period (FT), rainfall amount (mmR) in mm, the relative humidity (RH) in %, rainfall intensity (RI) in mm h^{-1} , wind speed (WS) in km h^{-1} and the number of days on which snow (SN), hail (Ha) and storm (ST) occurred. Not all variables were available for each sampling site. The x -variables that presented negligible information in modelling the calcium loss (Figure 2) were removed, and subsequently a new regression was performed. The equations for the reduced data set are shown in Table V.

Based on Figure 2, the blank concentrations of TSP, HCO_3^- and Na^+ , and SO_2 , temperature, relative humidity and the rain intensity were removed for UIA. Only the blank run-off volume and rainfall amount have a significant regression coefficient. NO_3^- , H^+ , K^+ , Ca^{2+} , SO_2 , NO_2 , dust, FT and RI were eliminated from the model for PML. At this site, the blank run-off volume and rainfall amount have a significant regression coefficient, together with the Mg^{2+} input, wind speed and unexpectedly the amount of snow days; Cl^- and Na^+ input, relative humidity and days of hail and storm also affect limestone mass loss. For PORT, HCO_3^- , SO_2 and C_nH_m do not contribute much to the model and were removed. In the resulting regression only the blank run-off volume, rainfall amount and SO_4^{2-} have a significant regression coefficient. H^+ , SO_2 , NO , O_3 , rain intensity and the number of snow and storm days were rejected from the PLS-model for SEA. Here, relative humidity, blank run-off volume, rainfall amount, Na^+ and SO_4^{2-} determine the stone loss. At OFF, H^+ , K^+ and rain intensity were eliminated from the regression, the stone loss is determined only by the blank run-off volume and rainfall amount.

Correlation coefficients (expressing measured versus predicted mass losses) for the damage functions were much better when applying PLS as compared to MLR, however, the regression coefficients of many variables were not significant. Taking into account that only calcium loss was considered to represent the mass weathering rate of lime stone, the intercepts had a significant contribution at all sites, as was also observed by Reddy and Youngdahl (1987). Atmospheric pollutants and acidity were not significant in predicting stone loss for short time intervals, which is in agreement with the findings of e.g., Benarie (1991); Webb *et al.* (1992) and Cooke and Gibbs (1993). Although the correlation coefficient was high for OFF, the contribution of the variables to the model was negligible. Only at PORT the input of SO_4^{2-} affected stone loss. Almost all variables controlled the calcium loss in the urban PML site. At SEA, the relative humidity influenced the material loss. No influence of sea salt particles was observed at SEA and only the input of Na^+ and SO_4^{2-} was significant, but not that of Cl^- or Mg^{2+} . In Table V experimentally and calculated calcium losses are compared to evaluate the quality of the regression. The results are satisfactory and better than those for the damage functions obtained

with MLR (error <1%). However, the quite large and significant intercepts prove that not all causes of the dissolution loss were identified.

3.3. POOLED REGRESSION

3.3.1. Pooled Mechanism Equation

A general mechanism equation was calculated to explain the calcium loss from the limestones, based on the ion concentrations found in the run-off water (subscript RO). For this purpose, data from all five sampling sites were pooled and subjected to PLS regression. In the resulting equation, given below, ion amounts are expressed in $\mu\text{eq}/\text{mcu}/\text{week}$. The significance of the variables is indicated with symbols, as is explained in Table II.

$$\text{Ca}_{\text{RO}}^{2+} = 280^{***} - 0.20 \text{H}_{\text{RO}}^{+***} + 0.45 \text{Cl}_{\text{RO}}^{-***} + 0.74 \text{NO}_{3\text{RO}}^{-**} + 1.1 \text{SO}_{4\text{RO}}^{2-***} + \\ 0.76 \text{HCO}_{3\text{RO}}^{-***} + 1.4 \text{Mg}_{\text{RO}}^{2+**} + 0.74 \text{Na}_{\text{RO}}^{+***} - 0.01 \text{K}_{\text{RO}}^{+ns} .$$

The correlation coefficient for this equation is 0.85. It seems that K^+ , Mg^{2+} and NO_3^- losses are not important in explaining the weathering mechanism. The overall decay mechanism is determined by the loss of SO_4^{2-} , HCO_3^- , Cl^- and Na^+ . This suggests that calcium loss of the limestones occurs mainly by dissolution of calcite, gypsum formation and action of (marine) salts. This last phenomenon was not evident from the individual mechanism equations of the sites separately. An estimation of the relative contribution of the separate variables was obtained by introducing in the average values of each sampling site. SO_4^{2-} had a high contribution in the polluted areas (60% at PORT and 40% at UIA and PML), HCO_3^- dominated at OFF (70%) and SEA (50%). The rain acidity contributed only a few percents to the limestone weathering at PORT, PML and UIA, while the contribution of the intercept ranged from 20 to 40%. The influence of the remaining variables was smaller than 5%. Only at SEA, a relatively high contribution (10%) of Na^+ and Mg^{2+} to the limestone loss was found. Since it is not possible to differentiate between the different weathering mechanisms when applying only one equation, a comparison between the calculated and measured calcium loss was made. The prediction error was smaller (1%) for the pooled regression compared to regressions based on individual sites (around 10%).

3.3.2. Pooled Damage Function

A general damage function was obtained by pooling the data from all five sites. The X-matrix contains the ion concentrations found in the blank run-off water (subscript TD), together with data covering atmospheric pollutants and meteorological parameters. Parameters that were not available for all sites were not included in this calculation. The resulting equation is shown below. Symbols are explained in Table II and variables are described in the 'sampling and analyses' section.

$$\text{Ca}_{\text{RO}}^{2+} = -130^{***} + 0.23 \text{Vol}_{\text{TD}}^{***} + 0.07 \text{H}_{\text{TD}}^{+ns} + 0.28 \text{Cl}_{\text{TD}}^{-***} + 0.16 \text{NO}_{3\text{TD}}^{-ns} +$$

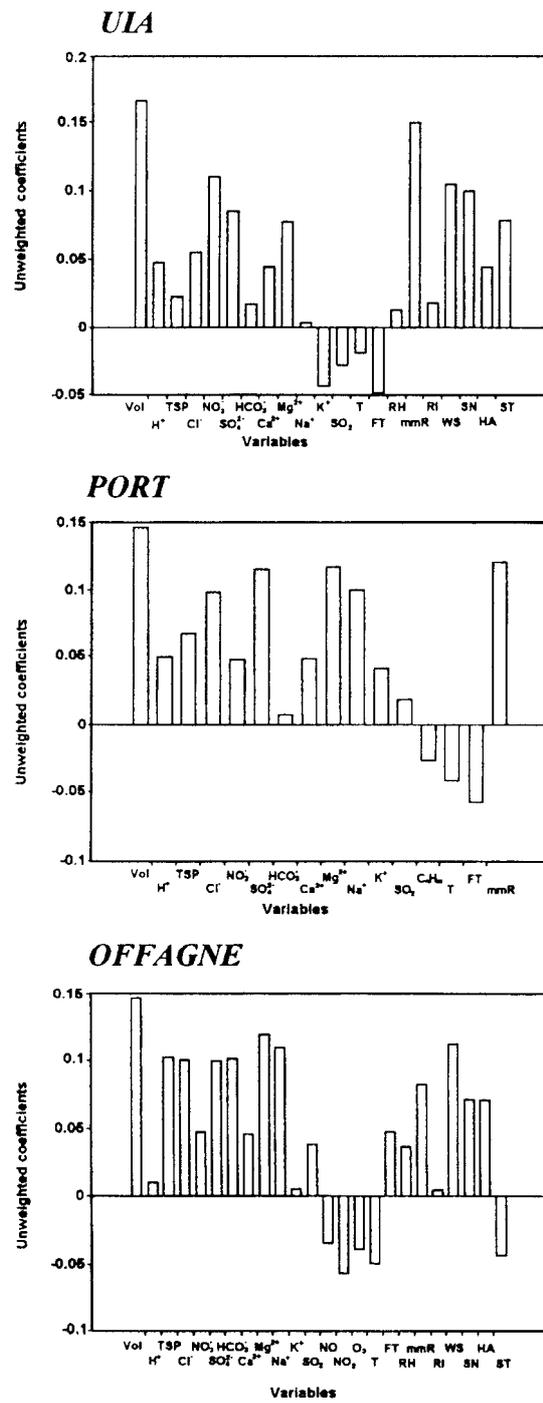


Figure 2. Graphical representation of the unweighted regression coefficients for the damage functions obtained by PLS regression in the five sampling sites in Belgium.

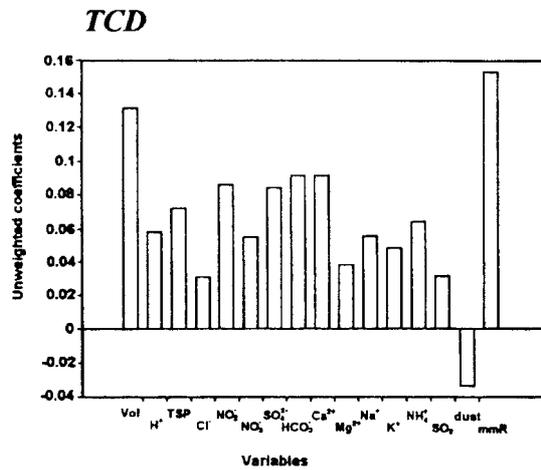
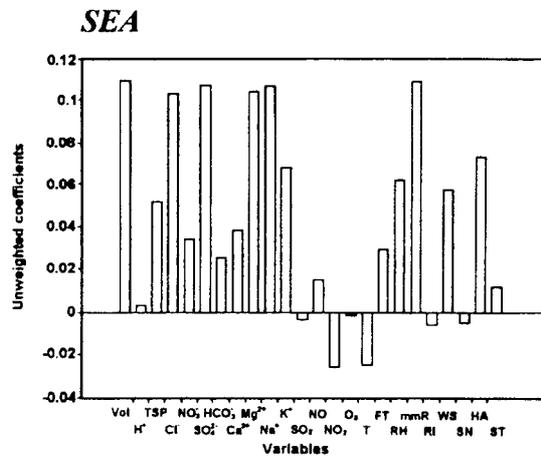
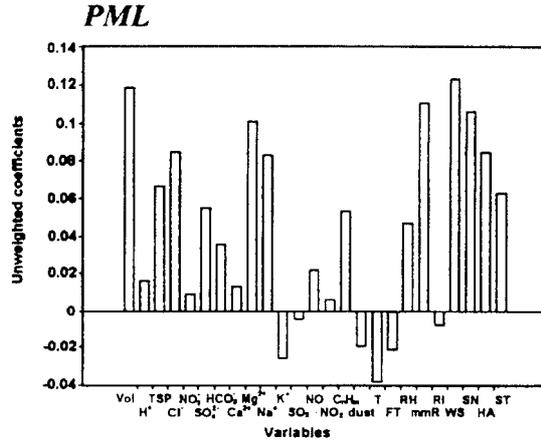


Figure 2. (continued)

$$\begin{aligned}
& 0.76 \text{SO}_{4\text{TD}}^{2-\text{***}} + 0.17 \text{HCO}_{3\text{TD}}^{-\text{ns}} + 0.31 \text{Ca}_{\text{TD}}^{2+\text{ns}} + 1.9 \text{Mg}_{\text{TD}}^{2+\text{***}} + \\
& 0.32 \text{Na}_{\text{TD}}^{+\text{***}} + 0.25 \text{K}_{\text{TD}}^{+\text{ns}} + 3.2 \text{SO}_2^{**} + 0.93 \text{NO}^{\text{ns}} + 0.56 \text{NO}_2^{\text{ns}} - \\
& 2.6 \text{T}^{\text{ns}} - 3.4 \text{FT}^{\text{ns}} + 3.2 \text{RH}^{\text{***}} + 6.2 \text{mmR}^{\text{***}} - 7.8 \text{RI}^{\text{ns}} - 0.10 \text{WS}^{\text{ns}} .
\end{aligned}$$

The correlation coefficient of this equation is 0.52, which is not as good as that for the mechanism equation and the individual damage functions obtained for each of the sites separately. The blank run-off volume, rainfall amount, relative humidity and SO_4^{2-} , Cl^- and Mg^{2+} concentrations determine the stone loss together with Na^+ and SO_2 . The mass loss rate of limestone is not simply correlated with the ambient atmospheric pollutant concentrations (Butlin *et al.*, 1985). Apparently, the rain acidity does not influence the stone loss, which is in agreement with the observations made by Cooke and Gibbs (1993). Introducing the average parameter values for each site separately into the equation above shows that the rain amount (Vol and mmR) determines up to 30% of the loss, the relative humidity more than 20% and the ambient SO_2 concentration more than 10% at UIA, PML and PORT, and around 5% at SEA and OFF. Na^+ , Cl^- , SO_4^{2-} and Mg^{2+} explain 30% of the material loss at SEA. For all sites, the contribution of the intercept amounts to 10%.

3.3.3. Restrained Pooled Damage Function

Since the variables do not have a similar importance in predicting limestone mass loss, a *restrained* pooled damage function was constructed, using only the most relevant variables. According to Webb *et al.* (1992) unrestrained regression analysis of the whole data set can lead to misleading results. PLS regression was performed to calculate a calcium loss prediction model, which only includes blank run-off volume and SO_4^{2-} together with SO_2 and H^+ , which appeared less important from the pooled damage function. The combination of these four variables leads to a prediction model with a correlation coefficient of 0.77, which explains 59% of the variance within the X-matrix. The resulting model is given below (ion concentrations are expressed in $\mu\text{eq}/\text{mcu}/\text{week}$, volume in $\text{mL}/\text{mcu}/\text{week}$ and SO_2 concentration in $\mu\text{g m}^{-3}$):

$$\text{Ca}_{\text{RO}}^{2+} = -29^{\text{***}} + 0.44 \text{Vol}_{\text{TD}}^{\text{***}} + 0.60 \text{H}_{\text{TD}}^{+\text{***}} + 2.0 \text{SO}_{4\text{TD}}^{2-\text{***}} + 5.5 \text{SO}_2^{\text{***}} .$$

Relative to the unconstrained model, the contribution of the intercept has decreased (3%), while the blank runoff volume determined up to 70% of the stone loss at OFF (a less polluted site), and 30% at PORT. Rain acidity contributes only 1% and up to 7% in the centre of Antwerp (PML). Although the contribution of SO_2 decreased for the less polluted sites (6% at SEA and OFF), no significant differences in the contribution of SO_4^{2-} were evident. In addition at the less polluted sites SO_4^{2-} accounts for 30%. The constrained pooled model results in a good prediction of the limestone calcium loss. Calcium loss is underestimated by 20% at OFF, whereas

TABLE VI
Damage functions from literature. See text for symbol explanations

Reference	Weathering rate	Damage function
Reddy <i>et al.</i> (1985)	$\mu\text{m}/\text{m}_{\text{rain}} \text{ yr}$	$4.88 + 0.0015 \text{ H}^+ (\mu\text{eq}/\text{m}^2 \text{ yr}) + 0.069 \text{ SO}_2 (\mu\text{g m}^{-3})$
Lipfert (1989b)	$\mu\text{m}/\text{m}_{\text{rain}} \text{ yr}$	$18.8 + 0.016 \text{ H}^+ (\mu\text{mol L}^{-1}) + 0.18 [v_d (\text{cm s}^{-1}) * \text{SO}_2 (\mu\text{g m}^{-3})]/\text{rain} (\text{m yr}^{-1})$
Baedecker (1990)	$\text{mmol Ca}^{2+}/\text{L}$	$0.16 [1.0 - 0.015 \text{ T} (\text{°C}) + 0.0000922 \text{ T}^2 (\text{°C})] / 0.683 + 0.49 \text{ H}^+ (\text{mmol L}^{-1})$
Webb <i>et al.</i> (1992)	$\text{g}/\text{m}^2 \text{ day}$	$-0.162 + 0.0058 \text{ SO}_2 (\text{ppb}) + 0.0666 \text{ Rain} (\text{mm day}^{-1}) + 638 \text{ acid} (\text{mol m}^{-2} \cdot \text{day}) - 0.0026 \text{ NO}_2 (\text{ppb}) + 0.0155 \text{ NO} (\text{ppb}) + 0.0007 \text{ O}_3 (\text{ppb})$
Kucera and Fitz (1995)	$\text{g}/\text{m}^2 \text{ 4 yr}$	$34.4 + 5.96 [\text{TOW}] * \text{SO}_2 (\mu\text{g m}^{-3}) + 388 \text{ Rain} (\text{m yr}^{-1}) * \text{H}^+ (\text{mg L}^{-1})$

at the other sites, the predicted values are within 5% of the measured calcium loss values.

3.3.4. Comparison with Damage Functions from the Literature

Many damage functions for calcareous stones have been published. Most of these functions are based on MLR and include only few variables. Five damage functions have been selected to compare their predicted limestone mass losses with the outcome of the model proposed in this article. Table VI shows the damage functions as originally published. To enable comparison between the different equations all functions were rearranged so that the units are similar: stone loss is expressed in $\mu\text{m}/\text{m}_{\text{rain}} \text{ yr}^{-1}$, pollutants in $\mu\text{g m}^{-3}$, ion concentrations in mmol L^{-1} and rain in m yr^{-1} , deposition velocities (v_d) in cm s^{-1} and T in $^{\circ}\text{C}$ (Table VII). Although absolute ion deposition amounts (mass/surface area.time) present a better description of the real deposition onto the stone surface (Steiger and Dannecker, 1994), in this work concentrations in run-off water were used since this measure is more generally used in the literature. Calcium loss expressed in g m^{-2} was converted to surface recession expressed in μm using an averaged value for the density of limestone, i.e. 2500 kg cm^{-3} .

Lipfert (1989a) used data by Reddy *et al.* (1985) to calculate a damage function for Indiana limestone exposed at three test sites in U.S.A., taking into account only atmospheric SO_2 concentrations and rain acidity. Reddy *et al.* (1985) exposed limestone slabs with an inclination of 30° , whereas the stone slabs in this work

TABLE VII

Adjusted damage functions, expressing surface recession rates in $\mu\text{m}/\text{m}_{\text{rain}} \text{yr}^{-1}$. See text for symbol explanations

Reference	Damage function
Reddy <i>et al.</i> (1985)	$4.9 + 150 \text{H}^+/\text{rain} + 0.069 \text{SO}_2$
Lipfert (1989b)	$18.8 + 0.016 \text{H}^+ + 0.18 v_d \text{SO}_2/\text{rain}$
Baedecker (1990)	$9.4 * [1.0 - 0.015 \text{T} + 0.000092 \text{T}^2] + 20 \text{H}^+$
Webb <i>et al.</i> (1992)	$150/\text{rain} * [-0.16 + 0.0020 \text{SO}_2 + 0.18 \text{R} + 1.7 \text{H}^+ * \text{rain} -$ $0.0013 \text{NO}_2 + 0.0086 \text{NO} + 0.0003 \text{O}_3]$
Kucera and Fitz (1995)	$0.1/\text{rain} * [34 + 6.0 [\text{TOW}] * \text{SO}_2 + 390 \text{H}^+ * \text{rain}]$
PLS pooled model	$0.015/\text{rain} * [-29 + 590 \text{rain} + 800 \text{H}^+ * \text{rain} +$
(this article)	$5300 \text{SO}_4^{2-} * \text{R} + 5.5 \text{SO}_2]$

were exposed with an inclination of 15° . Vleugels (1992) did, however, not find any significant differences in limestone mass loss with varying exposure angle (15° , 30° and 45°). Lipfert (1989a) postulated a damage function for generic limestone based on theoretical considerations concerning the kinetics of calcite dissolution when rain flows over the stone, attack by gaseous air pollutants, and acceleration of dissolution due to rain acidity. A deposition of 0.3 cm s^{-1} was used for SO_2 onto a limestone surface (Lipfert, 1989b; Cooke and Gibbs, 1993).

The damage function proposed within the NAPAP programme (Baedecker, 1990) was obtained from run-off water data of Indiana limestone samples exposed in New York. Webb *et al.* (1992) exposed small Portland limestone cubes at 13 sites in the United Kingdom. The mass loss from the stones was determined gravimetrically after one to three years of exposure. These authors used the percentage of limestone mass loss to estimate the rate of stone weathering, whereas the other studies mentioned above (including the study presented in this article) only take into account calcium dissolution, thus neglecting e.g., windblown losses. Webb *et al.* (1992) obtained an equation for the mass loss of limestone as a function of SO_2 , rainfall amount, rain acidity, NO_2 , NO and O_3 as the independent variables. Including NO , CO_2 and O_3 introduced a physically unrealistic negative value for the intercept. Kucera and Fitz (1995) proposed damage functions for several different materials, including limestones, using results of a four-year exposure study at 34 test sites in Europe, Canada and U.S.A. They defined the time of wetness (TOW) as the period of time when the relative humidity is higher than 80% and the temperature is above 0°C . For Belgium the TOW (defined in this way) lies around 0.6.

Table VIII shows the weathering rates for limestone, expressed as surface recession μm per meter rain and per year, calculated according to five damage functions selected from the literature, and the pooled damage function obtained with PLS

TABLE VIII

Comparison between measured (M) and predicted stone loss, expressed in $\mu\text{m}/\text{m}_{\text{rain}} \text{yr}^{-1}$, for the Massangis limestone exposed in Belgium. Predicted stone loss calculated according damage functions from literature and the proposed pooled (PLS) damage function model in this work (P)

Site	M	P	Reddy <i>et al.</i> (1985)	Lipfert (1989b)	Baedecker (1990)	Webb <i>et al.</i> (1992)	Kucera and Fitz (1995)
UIA	17.0	17.8	22.3	20.6	9.74	32.2	19.5
PML	18.5	19.0	27.8	20.5	10.2	23.1	21.1
PORT	29.0	27.0	29.8	22.5	10.1	47.9	35.3
SEA	15.2	15.4	11.8	19.4	8.71	8.31	9.62
OFF	15.5	12.9	13.9	19.6	9.04	14.7	11.0
Total	18.5	18.5	22.7	20.5	9.43	66.1	22.1

presented in this article. Predictions are compared with the measured surface recession rates. Limestone mass loss is best predicted with the damage function presented in this article. This is, of course, partly because the latter damage function was initially constructed as best fitting the data that is eventually used to compare the predictive abilities of the different equations. The NAPAP damage function (Baedecker, 1990) underestimates the surface recession of limestone by 50%. In the highly polluted harbour of Antwerp (PORT), the prediction error amounts 90%. These poor predictions are probably caused by the fact that the NAPAP damage function only considers rain acidity, not taking into account other deleterious factors. The surface recession rates predicted using the damage functions proposed by Reddy *et al.* (1985), Webb *et al.* (1992) and Kucera and Fitz (1995), show the same trend as the measured surface recession rates, with prediction errors ranging between 60% to less than 10%. Applying the model of Reddy *et al.* (1985) leads to a good prediction of the surface recession rates measured at PORT (2% error). On the other hand the model proposed by Kucera and Fitz (1995) leads to a better prediction of limestone surface recession rates in moderately to highly polluted environments such as UIA, PML and PORT (error 15%, but up to 40% at OFF and SEA). The model of Webb *et al.* (1992) adequately predicts the surface recession rate at OFF (5% error). As a consequence of the gravimetric determination of surface recession rates, larger predicted recession rates could be expected using this equation. The theoretical damage function proposed by Lipfert (1989b) leads to the best prediction of limestone surface recession rates in Belgium. The highest prediction error obtained using the latter equation is 30%, whereas for the other damage functions prediction errors larger than 50% were calculated. Lipfert's model permits to estimate the contribution of clean rain (in equilibrium with atmospheric CO_2 ; $\text{pH} = 5.6$), acid rain and SO_2 attack to the surface recession rate

of limestone. In Belgium, 70% (PORT) to 93% (SEA and OFF) could be attributed to the clean rain dissolution, 3% (SEA and OFF) to 15% (UIA and PORT) to acid rain and 4% (SEA and OFF) to 18% (PORT) to SO₂ attack.

4. Conclusions

The weathering mechanism of the Massangis limestone due to overrunning rain-water at five sites in Belgium can be explained as a function of the SO₄²⁻ and HCO₃⁻ loss. A high SO₄²⁻ loss from gypsum layers dominates at high polluted sites (e.g. Antwerp city), while a high HCO₃⁻ loss from dissolution of calcite controls the stone decay at the sea and an unpolluted Ardennes hillside. Only in the area around Antwerp, H⁺ loss is of some importance. NO₃⁻ loss does not contribute to the limestone mass loss. Damage functions calculated for the sites separately indicate that the rain volume is the major deleterious factor determining calcium loss. No straightforward short-term correlation between pollutant concentrations and calcium loss from limestone could be demonstrated, which is in agreement with the observations of many other researchers. Most probably because the atmospheric pollutant concentrations do not necessarily represent the delivery of pollutants to the stones. Moreover, since only short time dissolution loss of the stones was considered, given certain environmental conditions, the effect over longer time is not taken into account. Short-term correlation with pollutants may be obscured by retention of reaction products on the porous stones.

The pooled mechanism equations reveal dissolution of calcite, gypsum formation and crystallisation of salts as major weathering processes. The relative importance of these factors varies between the sites. The pooled damage function identifies the following deleterious factors as determining the weathering rate of limestone (in decreasing order of importance): the amount of rainfall, the deposition of SO₄²⁻ and salts, the SO₂ concentration and the humidity. The calculated calcium loss deviates from the measured loss by about 10%. PLS regression led to better results compared to MLR regression.

The damage function elaborated in the present work was compared with five damage functions selected from the literature. The pooled damage function obtained using PLS regression, proposed in this work, leads to the best predictions of limestone surface recession rates. Comparing different limestone damage functions selected from the literature and the one proposed in this work, has pointed out the need for standardisation of this kind of field exposure studies in order to make them more compatible.

Acknowledgements

This study was partially supported by the Commission of the European Community under contract no. EV4V-0052-B (GDF) and STEP CT90-0107.

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