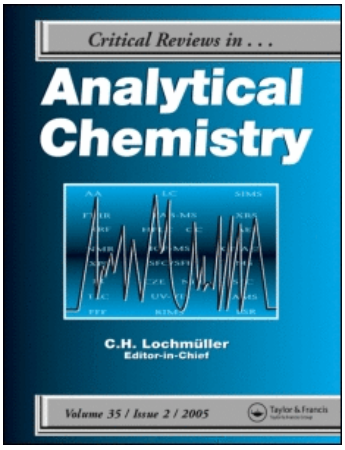

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THE INFLUENCE OF AIR POLLUTION ON THE MONUMENTS OF LATVIA

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Introduction

According to the data of the Environmental Protection Committee of the Republic of Latvia (1) the major part (65 - 68 %) of the listed air pollution is created by transport (see Tab. 1.)

Tab. 1. Distribution of emissions according to sources in 1992 and 1993.

Pollution source	Transport	Energy prod	Industry
year			
1992	65 %	26 %	9 %
1993	68 %	27 %	5 %

Main damaging gases for stone materials are SO_2 (mainly from oil- or coal- fuel power plants, the industry etc.) and NO_x (mainly from the traffic) (2). The chemical action to the lime-based binders, the capillary structure and sometimes to the reactivity of the aggregate which is destroyed at higher concentrations of the acids (3).

95 % of emission from stationary sources in Latvia registered in 1993 were created by the following: sulfur dioxide (50.1 %), nitrogen oxides (10 %), carbon oxide (2.4 %) and solid particles - ash (10.8 %) (1).

Table 2. shows how the number of traffic unites are growing in Latvia and what situation is aspected to be until year 2010 (5).

Table 2. The perspective of the number of transport unites until year 2010.

Type of transport, thousand	1990	1991	1992	1993	1995	2000	2010
cars	283	328	350	391	420	550-600	700-800
buses	12	13	18	20	15	20	30
lorry	67	71	75	85	xx	xx	xx

The air quality of Riga city

Riga the capital of Latvian Republic founded in 1201 is rich with it's old cultural heritage mainly located in the eldest part of the tow - Old Riga. One of the most beautiful objects of old city is Riga cathedral or so called Riga Dome Church. The other two object used as objects for observation and where the scientific investigations and practical stone restoration works are carried out - are no so old but important for the Latvian people as the symbols of their national identity. They are: Monument to Freedom (1935) and Riga Brethren's Cemetery (1924 - 1936).

The Monument to Freedom as well as Dome Cathedral are dislocated in the hart of city - in the center where a lot of traffic are going around. Riga Brethren's Cemetery a bit away in green district, but where fore some years ago he Superphosphate Factory was still in action (closed down in 1965) (4).

The air quality of Riga is measured by the specialists of the Riga municipal Environmental Protection Board, Air Monitoring Division. Thanks to the computerized system the amount of SO_2 and NO_x was registered in the region of those object and the results are depicted in Tab. 3. However the amount of CO_2 which also have a great significance in the processes of stone corrosion due to technical reasons had not been fixed. The amounts of SO_2 and NO_x were registered during the period 1993 - 1997. In Table 3 . the mean values and maximal amounts are given.

Table 3. The amounts of NO_x, NO_2 and SO_2 during the period 1993 - 1997, $\mu kg/m^3$

The amounts of NO_x, $\mu kg/m^3$

Object	winter, mean	winter, max.	summer, mean	summer, max.
Riga Dome Cathedral	100	748	80	330
Monument to Freedom	148	597	145	481
Riga Brethren's Cemetery	15	94	28	54

The amount of NO_2, $\mu kg/m^3$

object	winter, mean	winter, max.	summer, mean	summer, max.
Riga Cathedral	50	37	42	57
Monument to Freedom	56	33	56	37
Riga Brethren's Cemetery	11	45	13	75

The amount of SO_2, $\mu kg/m^3$

object	winter, mean	winter, max.	summer, mean	summer, max.
Riga Cathedral	1	12	0	0
Monument to Freedom	1	6	0	0
Riga Brethren's Cemetery	3	31	0.5	5

The influence of air pollution to the stone objects

Riga Dome Cathedral

The largest portion of stone objects of the Riga Dome (1211) are in the cross vaulted Cloister passages Exposed to weathering conditions and influence of air pollution. At the arched gallery of Riga Dome, dolomite (Sarema, Estonia) has been used for consoles, capitals and bases. This stone type have a slightly grayish color, which in some places occurs as darker spots. In some places small greenish spots can be observed. The full chemical analyses of this stone type is given in Tab. 4.

Monument to Freedom

Two stone types are used for the Monument to Freedom: gray and reddish granite from Finland and white Italian travertine. In this work more attention was paid to the travertine as it is type of limestone. The full chemical analyses of this stone material is given in Tab.4.

Riga Brethren`s Cemetery

There are several types of stone used in the construction of object: sandstone from Germany, local dolomite, Italian travertine and local limestone - tufa (Allaži). The most part of the sculptures and the covering blocks of walls are made from the last one. A small amount of organic substances (1.53 %) and Fe_2O_3 (o.11 %) are responsible for its yellowish color. Though very porous, it is, however frost - resistant, because the pores never fill up with water more than 90 % of the volume (4).

The Table 4. shows the chemical composition of all three stone types used for the construction of objects mentioned above. The analyses by the chemists of Riga Technical University were carried out.

Table 4. Chemical composition of dolomite (Riga Cathedral), travertine (Monument to Freedom) and tufa (Riga Brethren's Cemetery).

Chemical comp. % stone	heating loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
dolomite (Riga Cath.)	44.82	4.35	0.78	0.69	28.94	18.90	0.26	0.65	0.87
travertine (Monument to Freedom)	44.36	0.35	0.10	0.09	54.36	0.42	-	0.06	-
tufa (Brethr. Cem.)	4.05	0.68	0.15	0.11	52.80	2.06	0.30	-	-

Air pollutants are deposited to calcareous stone either in precipitation (wet deposition) or in dry form (dry deposition). Both wet and dry deposition of pollutants can cause significant deterioration of exposed stonework (7).

The basic chemical reaction is that sulfur dioxide, which when combined with atmospheric moisture, produces sulfur acid. This reacts with limestone and dolomite, producing gypsum and magnesium sulfate. In the presence of moisture, these salts penetrate the stone surface, collect soot, and begin recrystallizing. The stone surface is gradually covered with a black crust which cracks and peels off. Later the stone surface disintegrates in to powder, loses its mechanical strength and artistic form (8).

Most stone carvings are protected by roofs. Only sculptures in the Brethren's Cemetery and the Monument to Freedom are not - which is in advantage in that some of the corrosive agents are partly washed away by rain. Elsewhere, the situation is grave: the amount of sulfur trioxide on the surface of some carvings reaches 30 % of the surface's weight. The corroded stone surfaces display the following degrees of corrosion: I - black, mechanically strong upper layer with the largest sulfate contents (SO_3 - 15 - 36 %); II - the black, upper layer peels off, a powder-like disintegrated dolomite appears (SO_3 18 - 15 %); III - the stone carving has lost its artistic form (SO_3 8 %) (6).

The Table 5. Shows the amount of SO_3 on the stone surfaces which according to Vītiņa et al corresponds to the degree of corrosion.

Table 5. SO_3 on the surface of stone carvings

stone	SO_3 (%)	corrosion degree
dolomite (Riga Cathedral)		
- sample 1	22.60	II, III
- sample 2	24.20	I
- sample 3	7.20	III
travertine (Monument to Freedom)	8.00	solid surface; gray, slight gray
tufa (Riga Brethren's Cemetery)		
- sample 1	38.86	I
- sample 2	11.43	II
- sample 3	8.00	III

The relationship between sulfur amount on the surface and it's disintegrated state could be observed for the dolomite objects. The black but still solid crusts on mechanically strong stone surface are characterized by high sulfur contents.

In difference from dolomite and tufa, travertine is much more resistant to the influence of air pollution. No surface disintegration was observed for travertine objects and chemical analysis show (look Tab. 5.) low or no sulfur content on the surface.

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