Salt content of dust and its impact on the wall paintings of the church St. Georg at the UNESCO World Heritage site Monastic Island of Reichenau in Germany

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Abstract

St. Georg is one of the three Romanesque churches on the island of Reichenau at Lake Constance, Germany, built between the 9th and 11th century. UNESCO inscribed the monastic island of Reichenau in the World Heritage List in 2000. St. Georg has meticulously restored wall paintings which are exposed to a very humid indoor environment. Anthropogenic risks and preventive mitigation measures to reduce the environmental stress were identified within a research project. One aspect of research was the impact of salt in dust collected from time to time from different areas in the nave and the crypt. The paper identifies possible sources and analyses the harmfulness in relation to the indoor climate by salt mixture simulation with ECOS/RUNSALT. The data were compared with drilling samples of walls and passive dust sampling data. An experimental analysis by dynamic vapour sorption (DVS) of dust samples is planned in near fu-ture.

Keywords: Salts in dust, climate assessment, DVS, source identification, salt mixture analysis by ECOS/RUNSALT

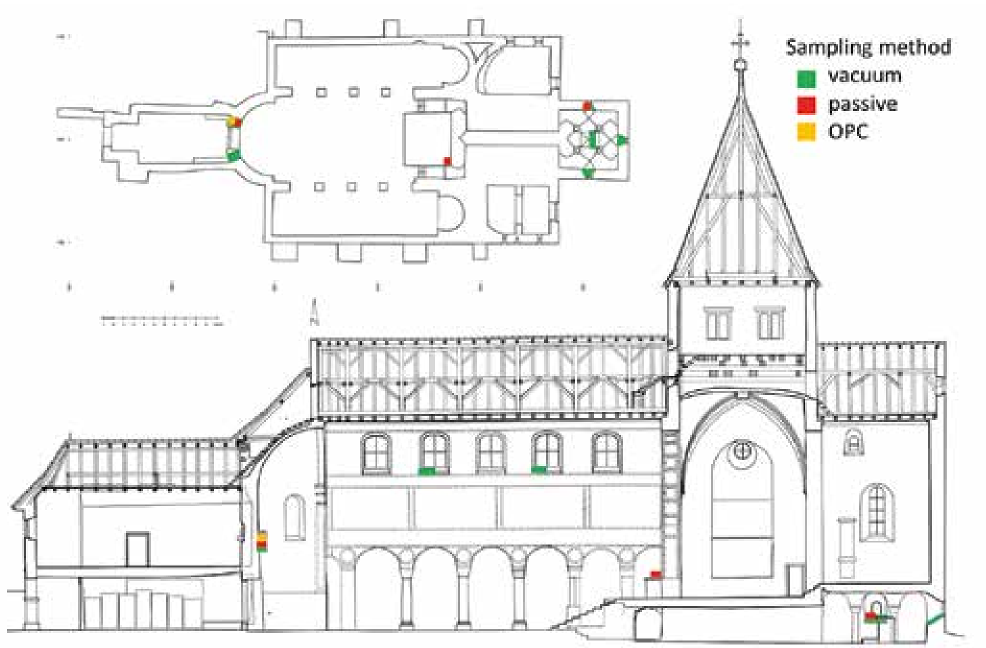

Figure 1: Sampling sites at St. Georg at the isle of Reichenau.

1. Introduction

In co-operation with the State Office for Monument Conservation Baden Württemberg, the Materials Testing Institute University of Stuttgart (MPA) initiated a national research project funded by the German Federal Envi-ronmental Foundation (DBU). The Project has started in 2015 with the aim of the identification of anthropogenic risks and preventive mitigation measures to reduce the environmental stress. One part was the collection and analysis of dust and fine-dust samples from time to time. Additional microbial volatile organic compounds (MVOC) sampling, fine-dust, CO_2 and climate monitoring and passive dust sampling was performed. See[1, 2, 3] for an overview. This paper will focus on the analysis of dust and fine-dust samples and the possible impact on the salt content on the wall paintings and walls in relation to the indoor climate.

2. Experimental

Dust samples were collected by vacuum cleaning on a quartz filter from several horizontal and inclined surfaces in nave, crypt and outside, mostly from window sills. Sampling intervals were monthly or longer. *Figure 1* shows the sampling sites. The samples were analysed by optical micros-copy and partly by ion chromatography and x-ray diffraction. Passive dust sampling on boron or carbon substrates and fine dust measurements with an optical particle counter (OPC, Grimm 1.109) were performed as well.

3. Results

3.1. Dust accumulation

The main series of dust samples was taken at the window sills of crypt and arcade windows of the west apsis. The accumulation differs with season with maximum values in autumn, see *Figure 1*. Additional samples from outside (crypt and cellar window sills) and nave (south and north upper window sills) were taken. *Table 1* lists the average values of dust accumu-lation for all sites.

The average daily accumulation of 6.1 to 6.8 mg/(m²d) is comparable for nave (west apsis) and crypt, except for the

Period	crypt east	crypt south	crypt north	west apsis north	west apsis south	crypt south exterior	crypt north exterior
	Average within period respectively in mg/(m²d)						
6.7.15-25.7.16	6,1	3,6	6,2	6,5	6,8	-	-
25.7.16-2.9.16	-	-	-	-	-	17	47,7
	nave south wall		nave north wall				
	west	east	west	east			
13.10.15-15.3.16	7,6	-	3,9	-			
15.10.15-16.3.16	-	3,7	-	2,9			

Table 1: Average values of dust accumulation for all sampled sites. The respective periods are given.

crypt south window with 3.6 mg/(m²d). The exterior samples (only one sampling period) showed higher values of 17.0 and 47.7 mg/(m2d). At the north and south wall of the nave an increase from east to west is visible *(Table 1)*.

3.2. Salt analyses

The salt content of the dust samples was analysed by ion chromatography. In *Table 2* the results for the two main series in crypt (east window sill) and nave

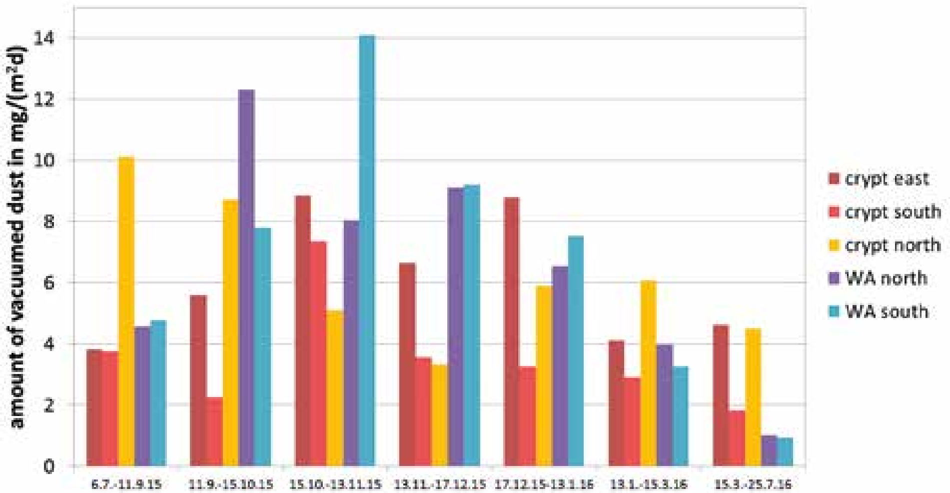

Figure 1: Dust accumulation of the main series in crypt (window sills) and nave (west apsis arcade windows sills).

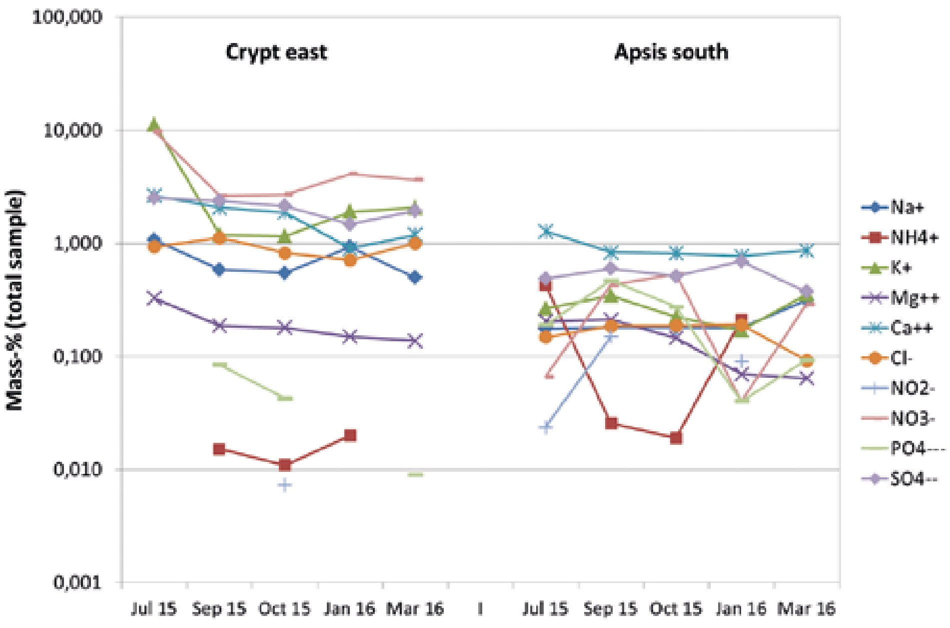

Figure 2: Salt analyses by ion chromatography of the two main series of dust collection.

(apsis south window sill) are given. A graphical interpretation of these results is shown in *Figure 2*. The first samples from July 2015 had a large collection time compared to the following samples, but the amount was comparable for most of the ions. Therefore within a short period of one or two months the salts were accumulated again.

In the crypt main ions were potassium, nitrate, as well as sodium, chloride and sulphate, whereas in the apsis higher concentrations of ammonia and phosphate occurred. Additional samples from window sills in the nave (north and south wall) showed nearly comparable results as the apsis sills *(see Table 4 in* [1]*)*, but with higher amounts of ammonium (around 0.2 to 0.9 mass-%). Especially samples from the north wall showed high amounts of nitrate (up to 0.9 mass-%) and oxalate (up to 0.3 mass-%).

Some dust samples from crypt and apsis were analysed by x-ray diffrac-tion. As expected calcite, gypsum and quartz occurred in both samples and some unspecific mixed crystals. *Figure 3* shows an analysis from the crypt with additional occurrence of niter. A sample from the apsis con-tained calcium oxalate hydrate.

Due to the lime plaster of the sills and walls it was not clear if the amount of calcium is due to the substrate. Additionally, some crystallized salts from the substrate could be in the collected dust samples. Therefore the fine dust collected in the filters of the optical particle counters (OPC) and dust samples from quasi neutral surfaces (organ, crypt altar) were collected and analysed. The results are shown in *Table 3* together with two samples from the outside window sills of the crypt. Due to the low amount of dust (1.2 to 1.7 mg) from the OPC filters, these values are less accurate.

On the filters high amounts of sodium, ammonium, sulphate and nitrite occurred compared to the main series *(Table 2)*. The amounts of calcium, potassium, magnesium and nitrate are comparable to the samples from the crypt series. Therefore salts from aerosol are a possible source.

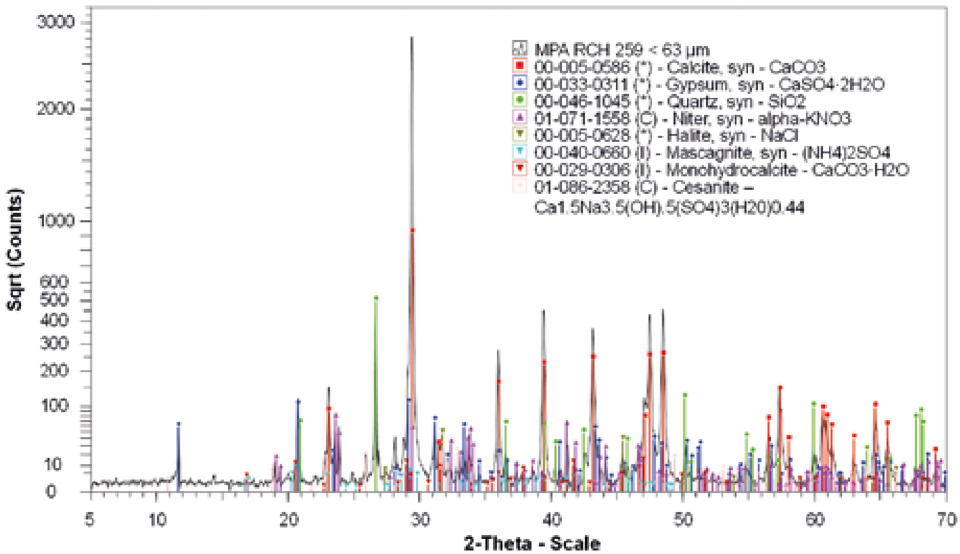

Figure 3: X-ray diffractometry of a dust sample from the crypt east window sill.

Positon/ Period/ Date	Na^+	NH_4^+	K^+	Mg_2^+	Ca_2^+
	mass-%	mass-%	mass-%	mass-%	mass-%
Crypt east					
06-07-15	1.07	< 0.01	11.30	0.33	2.64
06-07-15 – 11-09-15	0.58	0.02	1.19	0.19	2.07
11-09-15 – 15-10-15	0.55	0.01	1.16	0.18	1.87
17-12-15 – 13-01-16	0.93	0.02	1.90	0.15	0.90
13-01-16 – 15-03-16	0.50	< 0.01	2.07	0.14	1.19
Apsis south					
06-07-15	0.17	0.43	0.27	0.20	1.28
06-07-15 – 11-09-15	0.18	0.03	0.34	0.21	0.83
11-09-15 – 15-10-15	0.18	0.02	0.22	0.15	0.81
17-12-15 – 13-01-16	0.18	0.21	0.17	0.07	0.77
13-01-16 – 15-03-16	0.31	< 0.01	0.35	0.06	0.86

Positon/ Period/ Date	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	$C_2O_4^{2-}$
	mass-%	mass-%	mass-%	mass-%	mass-%	
Crypt east						
06-07-15	0.93	< 0.01	9.78	n.d.	2.52	n.d.
06-07-15 – 11-09-15	1.12	< 0.01	2.64	0.08	2.38	n.d.
11-09-15 – 15-10-15	0.82	0.01	2.70	0.04	2.13	n.d.
17-12-15 – 13-01-16	0.71	< 0.01	4.10	< 0.01	1.47	n.d.
13-01-16 – 15-03-16	1.00	n.d.	3.64	0.01	1.94	0.04
Apsis south						
06-07-15	0.15	0.02	0.07	0.19	0.49	n.d.
06-07-15 – 11-09-15	0.19	0.15	0.43	0.47	0.59	n.d.
11-09-15 – 15-10-15	0.19	< 0.01	0.53	0.27	0.51	n.d.
17-12-15 – 13-01-16	0.19	0.09	0.04	0.04	0.69	n.d.
13-01-16 – 15-03-16	0.09	n.d.	0.29	0.09	0.37	0.16

Table 2: Salt analyses by ion chromatography of the two main series of dust collec-tion. Top: Cations. Bottom: Anions. The end of period or the date represents the sampling date.

The quasi neutral sites are comparable to their counterparts in nave (organ and apsis) and crypt (altar and east window sill). Therefore crystallised salts from the walls could not be the only contribution to the salt content. The outside samples are comparable to the apsis samples with amounts of ammonium and phosphate but less sulphate and chloride. In general these sites are not protected from rain; therefore some dissolution of salts could occur.

4. Discussion

The discussion will focus on the risk potential for the precious wall paintings and possible sources of the salts.

Positon/ Period/ Date	Na^+	NH_4^+	K^+	Mg_2^+	Ca_2^+
	mass-%	mass-%	mass-%	mass-%	mass-%
OPC-Filter					
Crypt 01-09-16 – 20 10-16	1.9	3.1	1.2	0.3	3.3
Apsis north L 01-09-16 – 20-10-16	1.4	2.1	0.8	0.2	2.2
Apsis north D 01-09-16 – 20-02-17	2.7	1.6	2.2	0.2	1.8
Organ 01-09-16 – 20-10-16	1.6	2.4	1.0	0.2	2.4
Extra sites					
Organ 02-09-16 – 24-03-17	0.79	< 0.01	0.21	0.07	1.29
Crypt altar 24-03-17	0.34	< 0.01	0.30	0.09	1.68
Crypt south outside 02-09-16	0.16	0.50	0.13	0.05	0.64
Crypt north outside 02-09-16	0.19	0.76	0.27	0.06	2.15

Positon/ Period/ Date	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	$C_2O_4^{2-}$
	mass-%	mass-%	mass-%	mass-%	mass-%	
OPC-Filter						
Crypt 01-09-16 – 20 10-16	0.4	0.6	3.9	0.1	10.2	0.9
Apsis north L 01-09-16 – 20-10-16	0.3	0.2	2.1	0.1	6.8	0.5
Apsis north D 01-09-16 – 20-02-17	0.2	0.2	2.4	0.0	6.3	0.0
Organ 01-09-16 – 20-10-16	0.2	0.5	2.6	0.1	8.5	0.6
Extra sites						
Organ 02-09-16 – 24-03-17	0.06	n.d.	0.21	0.02	0.57	0.10
Crypt altar 24-03-17	0.58	n.d.	1.77	< 0.01	2.52	0.02
Crypt south outside 02-09-16	0.09	0.02	0.03	0.22	0.26	< 0.01
Crypt north outside 02-09-16	0.07	0.17	0.03	0.25	0.30	< 0.01

Table 3: Salt analyses by ion chromatography of dust samples from OPC filters, quasi neutral sites and from outside. Top: Cations. Bottom: Anions.

4.1. Risk potential

The measured salt content of the dust is relevant and due to the accumula-tion of around 6 mg/(m²d) it is a continuous source for salts. The indoor climate is relatively humid therefore a solution of salts is possible which could be collected by the porous wall structure. To estimate the risk poten-tial a simulation of the possible salt mixtures was performed with the soft-ware ECOS/RUNSALT.[4] Two samples from crypt and apsis of known sampling periods and a third sample of drill dust (0 to 0.2 cm depth) from the east wall of the crypt near to window sill (analysis taken from[5]) were chosen. RUNSALT works with a limited number of ions and gypsum should be removed in advance due to the low solubility. Therefore the fol-lowing steps were performed to generate ion balanced data for the different samples:

1) Calculation of mole data out of the analyses.

2) Treatment of nitrite, ammonium and phosphate: In case of the crypt samples the amount could be neglected. In case of the apsis sample this was not possible. In a first step nitrite was added to nitrate which keeps the charge and the particle number but changes the mass. The next step was the calculation of the charge sum of am-monium and phosphate because ammonium phosphate is one of the main salts for these ions. In our case the amount of ammonium was higher therefore nitrate and sulphate (as well cations of major ammonium salts) were reduced accordingly. The results are sets of ECOS/RUNSALT compatible ions.

3) Adjustment of charge sum to zero. Carbonate could not be detect-ed by ion chromatography because for the anion analysis a hydro-gen carbonate/ carbonate solution is used as eluent. The assump-tion was that the charge difference is mainly due to calcium and

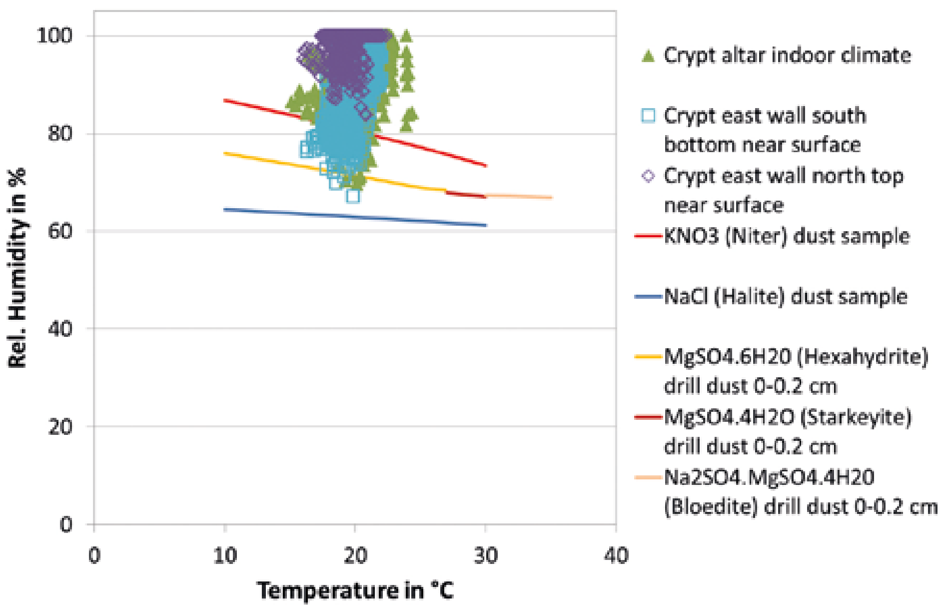

Figure 4: Comparison of simulated deliquescence humidities with climate data of the dust sampling period (6th July 2015 to 11th September 2015) in the crypt.

therefore the calcium content was reduced accordingly.

4) The last step was the removal of gypsum from the data due to the low solubility. The result is a set of data with either calcium (apsis, crypt drill dust) or sulphate (crypt) set to zero.

Figure 4 shows the deliquescence humidities for the different simulated salt mixtures for the sampling period from 6th July 2015 to 11th September 2015 in the crypt in comparison with the climate data of the same period. It could be clearly seen that in most of the time all salts in the dust are in so-lution and a lot of phase changes occurred for KNO_3 (Niter). The drill dust sample which represents the wall surface would have some phase changes for hexahydrite in that period.

In *Figure 5* the results of simulation for the apsis sample are shown. The sampling period was from 17th December 2015 to 13th January 2016.

As for the crypt sample the salts are mostly dissolved. Phase changes oc-curred for the three salt mixtures mirabilite, aphthitalite and picromerite.

The simulations show that salt solutions occur in the crypt as well as in the nave which could penetrate into the porous walls. Therefore there is a risk of continuous salt accumulation in the whole church. The risk is higher in the crypt due to the higher salt contents in the dust there. Two samples from nave and crypt were treated by dynamic vapour sorption (DVS), but the subsequent analysis by ion chromatography is in preparation. This will give information about the viability of simulated data.

4.2.Salt sources

The relatively high amounts of salts in the filter of the OPCs indicate that aerosols could contribute to the salt content in the dust. In the region of Baden-Württemberg[6] fine dust collected outside

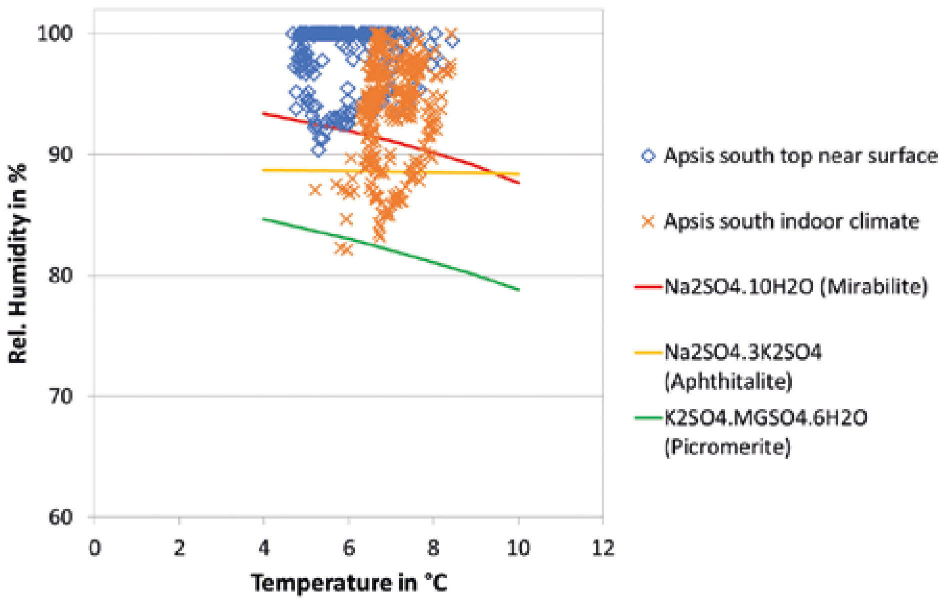

Figure 5: Comparison of simulated deliquescence humidities with climate data of the dust sampling period (17th December 2015 to 13th January 2016) in the ap-sis.

at different sites and periods was examined. Ammonium salts (nitrates and sulphates) occurred in percentages from 25% (high traffic street in Stuttgart) to 48% (Mann-heim urban background) and 51% (Black forest rural clean area). The sources are secondary aerosols formed from gaseous NO_x and ammonia in the atmosphere. In [1] the deposition rates in St. George were compared with data from a sheltered outside position (clock tower of Christchurch in Mainz).[7] The outside rates are 5 to 100 higher than in St. George which is not amazing due to the traffic surrounded site. This are hints that secondary aerosols are one of the sources for salts in the dust.

Another source could be salts from agricultural use. The Reichenau island is intensively used by agriculture. In [1] a calculation was performed by one of the authors (Weinzierl) which showed that nitrates from agriculture could contribute only to a minor part. The calculated amount of nitrate of 0.013 mass-% is small compared to inside values and only comparable to the outdoor samples *(Table 2 and 3)*. On the other hand the loose bound ground contains fine silt which could easily blow off by wind erosion. Sili-cate rich particles are one of the major compounds detected with passive sampling.[1, 2]

The higher amount of nitrates and sulphates in dust samples from the crypt *(Table 2)* might be due to the uptake of crystallised salts from the wall dur-ing sampling. There is as well a difference on quasi neutral surfaces (organ and crypt altar) visible, but on wall samples the difference is bigger *(compare Table 3)*.

There are several ways for aerosols to enter the church. One is the auto-matic opening of windows to control the climate in nave and crypt. Another source is the visitor traffic (only the nave could be visited). During the summer period (May to September) the visitor traffic is restricted to guided tours. The entrance hall serves as sluice, only when the front door is closed the groups enter the nave by a second door. But due to the high interest as UNESCO world heritage the church has large amounts of visitors. Typical dust from visitors is textile and biological particles as well as dust from the surrounding area from the shoes. The lower amounts of salts in the dust samples of the nave compared to the crypt *(Table 2)* might have their ex-planation in the additional dilution by non-mineral dust from visitor traffic.

5. Conclusion

The salt content in the dust contributes to the salt content of the walls due to solution processes according to the climate conditions. Due to the con-tinuous accumulation of dust (around 6 mg/(m^2d), *see Table 1*) it could increase the salt content in the walls over time and could be harmful to the precious wall-paintings. The ECOS/RUNSALT simulations show the poten-tial risks for the walls. Main sources of the salts in the dust are aerosols and input from visitor traffic. In the crypt some recrystallized salts from the walls could contribute as well.

It was suggested to keep the regulations for the visitor traffic in the summer period. Further research is needed to estimate the accumulation of dust by the automatic window opening for climatisation. It is planned to evaluate sedimentation rates and flow conditions.

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Geologie, Rohstoffe und Bergbau (LGRB) im Regierungspräsidium Freiburg", Robert Lung, Corinna Luz, tourism office and catholic congregation of Reichenau.

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