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Using paper pulp poultices in the field and laboratory to analyse salt distribution in building limestones

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Abstract

We investigated the behaviour of salt solutions during the drying process in porous stone and the extraction of salts by paper pulp poultices (PPP). The investigations were carried out at a 300 year old boundary wall of the Worcester College in Oxford, UK, as well as under laboratory conditions. The laboratory blocks of porous, bioclastic limestone (Aflenzer stone, Austria) were cut into stone cubes and prisms (5 × 5 × 5 and 5 × 5 × 20 cm) and soaked first with ultrapure H_2O and second with different concentrations (0.1, 0.5 and 1 mol l^{-1}) of a saline solution of NaCl and Na_2SO_4 to determine their behaviour during the dehydration process under different conditions. After determining the capillary absorption coefficient and the capillary rise behaviour of the stone cubes, we sampled material by PPP and by drilling. The samples were immersed in ultrapure water and the salt ion content was measured via conductivity and ion chromatography (IC). The main aim of the laboratory analysis was to investigate the effectivity of the PPP in extracting salts from the stone and to derive a semi-quantitative calibration (PPP results vs. original salt content). The field work at the college boundary wall comprised sampling (PPP and stone surface material) at surfaces of different weathering features. Finally, the field work results were compared to the laboratory work. The lab experiment results show that approximately 24% of the salts within a 100% saturated stone cube moved into the poultice within the 1 h of application. At 75% and lower saturation degrees, only 14–11% of the salts moved into the respective poultices. For the field setting, the amount of anions extracted by PPP is 6–63% (mean 20.7%) of the amount found in the stone samples. The spatial distribution of salt ion concentrations, collected by poultices, corresponds with the 'hot spots' of weathering.

Keywords: Salt weathering, Non-destructive method, Case study, Cultural heritage preservation, Stone decay

Background

Decay of building stone causes considerable damage and costs worldwide [1] and the problem will be amplified in some regions of Europe by ongoing climate change [2, 3]. Higher moisture levels in winter and increasing evaporation in summer are the most important influencing factors [4] determining salts and moisture contents which are among the most important agents of weathering. Sampling of salts under field conditions and thus, assessing the spatial distribution of damaging salts in building structures is still a difficult task. A possible, non-destructive sampling method is the application of so-called paper pulp poultices (PPP), a patch of wet cellulose fibres which is attached on the stone [5–8]. This method is frequently used as a desalination treatment in the context of building conservation. However, systematic investigations on the sampling effectivity and on the degree of salt movement from the stonework into the poultice have rarely been carried out (e.g. [5, 6, 8–11]), the focus being on semi-quantitative analysis and spatial distribution of salts sampled by PPP [5, 9, 10, 12, 13]. Also, basic technical instructions regarding the repeatability and comparability of measurements (e.g. the duration of application of the PPP) are lacking.

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Aims of investigation

The presented investigation is part of a longer-term project which deals with salt and moisture dynamics in weathered limestone walls. The main object of investigation is a part of the 300 year old boundary wall of the fellow garden of the Worcester College in Oxford, UK. In the current paper, we take aim on three points:

- To investigate the behaviour and distribution of water and salt solution of known concentration in porous stone at different saturation states under laboratory conditions;
- To verify the mechanism, reliability and quantify effectivity of salt sampling by paper pulp poultices;
- To compare the results of the laboratory analysis to those of the field campaign to achieve (semi-)quantitative information on salt concentrations.

Scientific background

There are two stages of drying of a wet, porous material. During the "externally limited drying stage" [14] the moisture transport is achieved by continuous capillary flow to the the drying surface. At the surface, the moisture evaporates due to the contact to the dry air circulation. The second stage is the so called "internally limited drying stage" in which the supply of water decreases, the capillary flow slows down and air spreads within the larger pores where the capillary pressure is lowest. The pores filled with liquid form isolated structures between the vapor filled pores [11, 14].

Liquid moisture is the transport media for dissolved salt ions. During drying, the ions move towards the drying front by capillary flow (advection) and accumulate near the surface. Gradually, a concentration gradient of ions develops and diffusion starts to balance the ion concentration inside the material. The location of the drying front depends on the supply of moisture from inside the material and on the evaporation rate at the external surface. If diffusion is the dominating process, the drying front is located in the subsurface of the material and salts will crystallise as sub-florescence. If advection prevails, the drying surface lies at the external surface of the material and salts will crystallise as efflorescence [14]. Therefore the area of salt crystallisation, sub-florescence or efflorescence, can give evidence for the kind of process taking place [11].

The poultice/substrate system describes an interaction between two porous materials in hydraulic contact. Processes like dissolution, diffusion and crystallisation are involved near the interface [8]. The mode of operation depends on environmental conditions (humidity, temperature, wind speed), properties of the materials (composition, porosity and pore-size distribution) and the presence and distribution of liquid and vapor phases inside the substrates [7, 11]. The pore-size distribution is of particular importance for the moisture and ion transport during the drying period, because moisture and ions move by advection from coarser to finer pores. Large pores provide water, while small pores extract salts during drying [7, 11, 15–17].

When applied, the cellulose poultices (PPP) are soaked with deionised water. The primary "wetting phase" thus represents the movement of moisture from the wet poultice into the substrate, where the extra water causes the solution of present salts. In the second phase, the "salt extraction", the dissolved ions move as saline solution from the substrate into the poultice. This transport is able to take place in two different ways. Advection forces the salt transport from the substrate to the poultice through capillary water flow which is a relatively quick process. The second, slower process is called diffusion and transports salt ions from the substrate into the poultice due to an unbalanced salt ion concentration gradient (Fig. 1). To maintain this process the poultice has to stay wet [17, 18]. To force capillary moisture flow during the drying process, the substrate has to consist of larger pores than the poultice, because the direction of water movement by advection is from coarser to finer pores [15–17]. Cellulose poultices possess mainly fine pores (see "Methods" section).

Methods

The approaches in field were carried out at the boundary wall of the Worcester College. The east-oriented wall side is located at a heavily used road and the west-oriented wall side is facing the fellow garden of the college.

Stone samples

The laboratory samples consist of limestone, the so-called Aflenzer stone of Austria, which is a bioclastic packstone with a grain size of $\leq$2.0 mm. In view of its fabric and composition, the stone is quite similar to the Cotswold stone building up the Oxford field site. The Aflenzer stone is porous, weakly cemented, rich in fossils and has a high percentage of calcium carbonate (>90%). Its apparent density ranges from 1.68 to 1.96 g cm^{-3} and its total porosity amounts 28–35% [19–21]. The samples were cut with a saw on all six sides, for most of the experiments into 5 × 5 × 5 cm cubes and for the capillary rise test we used prismatic stone samples of 5 × 5 × 20 cm. The Aflenzer stone block originated from a subterranean quarry, so it is a fresh, non-weathered stone.

The boundary wall of Worcester College consists of different fossiliferous bioclastic limestones of Jurassic age from Cotswold and from the surrounding of Oxford (Great and Inferior Oolithic Group). The oolitic

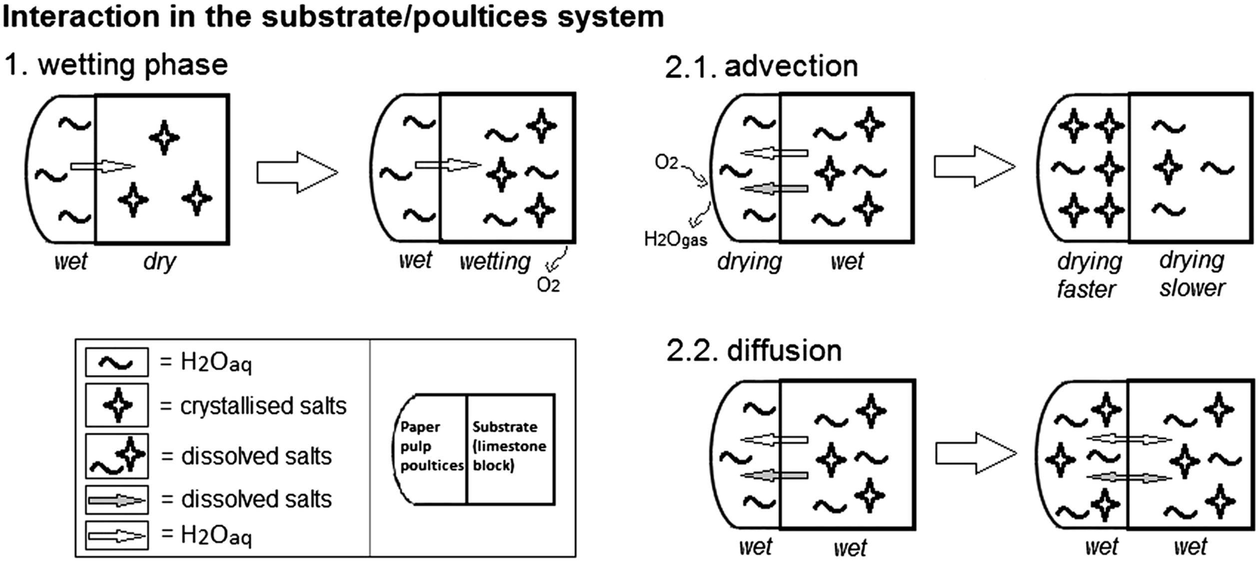

Fig. 1 Interaction of moisture and salt ions in the substrate/poultices system (own draft inspired by [7, 11, 14, 18]

bioclastic limestone blocks are also porous (1.90–1.99 g cm^{-3}), exhibit a similar grain size of $\leq$2.0 mm and are rather heterogeneous in view of their fabric and content. Weathering phenomena, like disintegration, cavernous weathering or crumbling, are preferentially visible at stone blocks which are very fossiliferous, porous and weakly cemented.

Laboratory investigation

To form the basis for the following approaches, the water (EN 1925) and salt solution absorption coefficient by capillarity [kg m^{-2} $s^{-0.5}$] and the capillary rise behaviour of the limestone samples were analysed. Then, the cubes were immersed under air pressure for 24 h in various liquids. For the first run, ultrapure H_2O was used. For subsequent runs, $NaCl/Na_2SO_4$ solutions of different concentrations (0.1, 0.5 and 1 mol l^{-1}) were applied. During the ensuing dehydration process samples were analysed at different states of saturation. Saturation levels were approximately 100, 75, 50, 25, 10 and 0%. Fully saturated samples are described as “100% saturated” in the following, although our method captures only the apparent (accesible) porosity. Three samples were used for each saturation level to get more significant results in each run. The first sampling session started after 24 h of immersion treatment. At this point, the stone cubes were fully saturated. On the next day, after approximately 24–36 h of drying (depending on the different stone characteristics) the 75% saturation level was reached, and so on. The stone cubes were weighed to find out the actual remaining water content immediately before sampling. Salts were sampled by drilling as well as by non-destructive application of PPP on the stone surfaces of the cubes. The sampling resultants (drill dust and poultice, respectively) were dissolved in deionised water and analysed with a conductivity sensor (WTW Cond 315i; measurement accuracy: 0.5% at 0…35 °C) and by means of Ion Chromatography (Dionex ICS-3000 Reagent-Free IC, Institut of Applied Geoscience, Graz University of Technology).

Furthermore, a test run with 35 stones soaked with a $NaCl/Na_2SO_4$ solution was performed. On each set of five stones, PPP were applied and removed after different elapsed times (10 min, 1, 3, 5 and 24 h). The PPP were treated as described below and the conductivities of the extracted salt solutions were measured. The aim of this experimental run was to investigate the influence of application time on the results.

Sampling by paper pulp poultices

Paper pulp poultices (PPP) consisting of cellulose fibers were used for non-destructive salt sampling. We used the so-called “Arbocell BC1000”; the pore size distribution of this type of cellulose poultices is 10–30 µm [6]. For each poultice used in the lab 3 g of material were used. After soaking in de-ionised water with a pulp-to-water weight ratio of about 1:20, they were applied for 60 min to the surface of the wet stone cubes (5 × 5 × 5 cm), usually covering one side of the cuboids almost entirely (Fig. 2a). The poultices were then removed, immersed in 60 ml deionised water and filtered to remove the remainings of the poultice [10, 13, 22]. After measuring the electrical

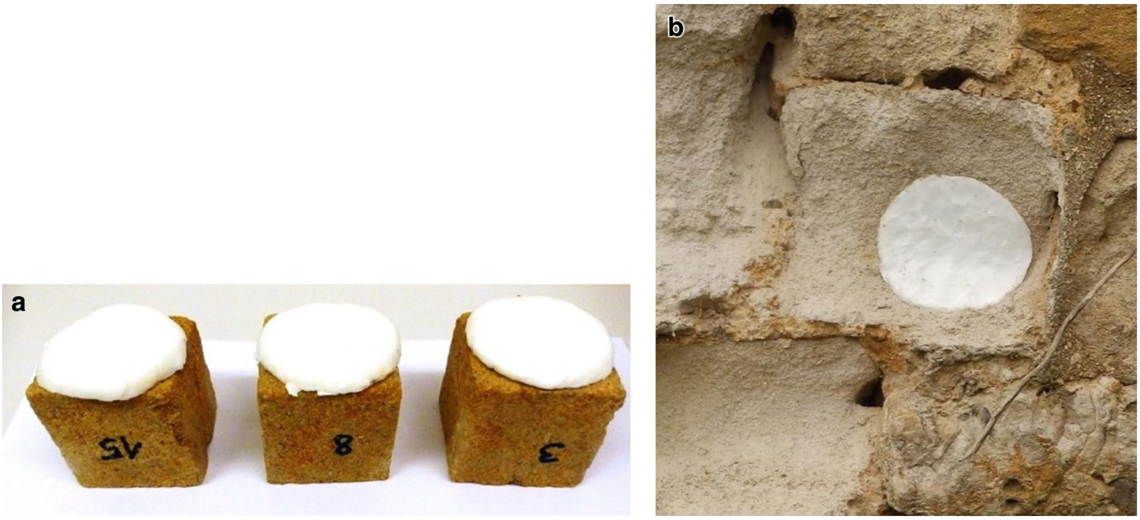

Fig. 2 **a** Application of poultices on the stone cubes under laboratory condititons; **b** application of poultices at the boundary wall, Worcester College

conductivity of the saline solution with a conductivity sensor (as a proxy for salt content), the samples were analysed by ion chromatography (IC).

Sampling by drilling

Prior to this sampling method the stone cubes were treated only with ultrapure H_2O and with 0.5 mol l^{-1} saline solution of NaCl and Na_2SO_4. We drilled into the stone cubes with a diameter of 8 mm up to a depth of 2 cm to detect the distribution of the salt solution within the stone. The drilling material was collected across depth intervals of 0.5 cm from the stone surface up to 2 cm depth. A certain amount of the stone powder was resolved with ultrapure water (1:10), shaked for 1 h, filtered (45 μm filter size) and measured by a conductivity sensor and further analysed by ion chromatography (IC). This destructive method was used to verify the quality and reliability of the sampling by PPP. To make the two methods (PPP and drilling) better comparable, the poultice results were later treated with a correction factor accounting for the much higher area of PPP sampling (approx. 13.7 cm^2) compared to the size of the drillhole (approx. 0.79 cm^2) resulting in a factor of approx. 17:1.

Field investigation

The PPP were used in the same way as under lab conditions, except a higher amount of cellulose fibers (9 g). The PPP were soaked in de-ionised water with the same pulp-to-water ratio as in the lab and applied to the sampling points for 60 min (Fig. 2b). The poultices were then removed, soaked in 180 ml of deionised water and filtered to remove the poultice. The anions and cations of the samples were investigated at the ion chromatograph. We applied the PPP in a grid of 8 × 8 with a distance of around 40 cm between the poultices. The grid thus covered an area of about 2.8 × 2.8 m and covered the most important weathering features like cavernous weathering, disintegration, crumbling and black crusts, as well as blistering and salt deposits. Drilling was not possible for reasons of monument protection; thus, we sampled by collecting detached stone material from the wall surface. The stone material was grinded, prepared analogous to the drill samples and investigated by ion chromatography (Dionex IC DX500 Chromatograph, Oxford Rock Breakdown Laboratory) to measure the salt amounts of the stone surface. The samples were taken along one vertical and one horizontal PPP profile.

To facilitate the reading flow we designate different kinds of salt solution concentration as follows:

- "Pore water concentration (or conductivity)": this is the ion concentration (or conductivity) in the pore water or in the applied salt solution, respectively;
- "PPP concentration (or conductivity)": This is the concentration (or conductivity) of the solution generated by dissolving the poultice in deionised water.

Results

Laboratory investigation

The water and salt solution absorption coefficients by capillarity (g m^{-2} $s^{-0.5}$) were measured for six samples and show a good accordance between the samples. The fluid uptake of the stone cubes ranges from 25.27 to 28.99 g m^{-2} $s^{-0.5}$ (water) and from 23.67 to 28.05 g m^{-2}

$s^{-0.5}$ (salt solution) within 72 h. The absorption coefficient by capillarity of Aflenzer stone are within the wide range of other stones used for salt sampling, e.g. c. 115 g m^{-2} $s^{-0.5}$ for Ançã limestone [10]; c. 15.36 g m^{-2} $s^{-0.5}$ for Moca Creme stone or 10.8 g m^{-2} $s^{-0.5}$ for Semirijo stone of Portugal [23].

The rate of capillary rise in the stone cuboids lies between 0.18 and 0.20 cm $s^{-0.5}$ (water) and between 0.19 and 0.22 cm $s^{-0.5}$ (salt solution). This result illustrates that the used stone cubes are well comparable to each other with small variability between the samples.

Paper pulp poultices

The investigated stone cubes were treated with different $NaCl/Na_2SO_4$ pore water concentrations. The amount of substance (mol l^{-1}) is well mirrored by the range of the measured conductivity values (µs cm^{-1}). The PPP conductivity shows an increasing trend from stone cubes with a low saturation level to the fully saturated examples. The highest PPP conductivity was measured at the approximately 100% saturated samples, strongly decreases at 50% saturation, and then follows a slightly falling curve down to 10% saturation of the stone cubes. Samples immersed by ultrapure H_2O can be used as a base level because the conductivity values are very low and show almost no difference between different saturation levels (Fig. 3). This means that hardly any soluble salts are provided by the stone itself, because the samples immersed by ultrapure H_2O show only approx. 4.25 mg l^{-1} chlorides and approx. 6.51 mg l^{-1} sulfates.

The "application time" test run shows that the results vary considerably between different durations of PPP application. Figure 4 shows the mean result of seven test runs. On average, the shortest application (10 min) delivered the highest PPP conductivity. The conductivity decreased with time down to a minimum at 5 h while the 24 h application delivered much higher values again. This means that the highest amount of salt is mobilised in the first salt extraction phase, probably because the salts tend to be concentrated near the surface (see lab results—drilling). The high values at 24 h can be explained by increasing capillary suction during the drying phase.

The optimal application time depends on the material, as well as on environmental conditions. The first transport of soluble ions from the substrate to the PPP initiates within 6–15 min [24]. This correlates to the "salt extraction" phase, described by Voronia [18] due to the interaction of the substrate/poultice system.

Based on these results, the application time of 1 h was chosen for the other test runs for the following reasons: (1) We assume that to extract salts, water has to move into the stonework and the saline solution has to move outward into the poultice *at the rate of capillary rise* (this

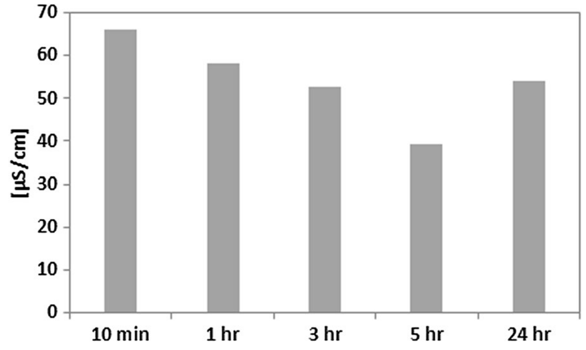

Fig. 4 Mean PPP conductivity result of test runs with different application times of PPP on stone cubes

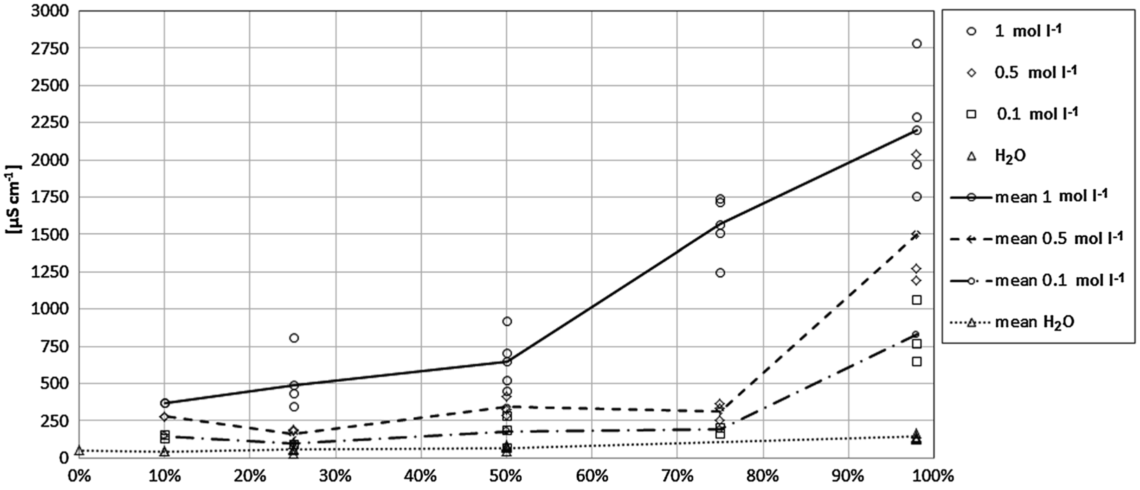

Fig. 3 PPP conductivity (µs cm^{-1}) at different saturation levels (%) from stones treated with different pore water concentration (mol l^{-1})

simplified view does not take diffusion processes into account of which the velocity is unknown). Based on a mean rate of capillary rise of 0.2 cm $s^{-0.5}$, water can move 4.9 cm within 10 min, which means approx. 2.5 cm in and 2.5 cm out. Thus, the depth of salt extraction is 2.5 cm at maximum. In 60 min the possible depth of salt extraction increases to 6 cm. We decided that this is a reasonable penetration depth in the field which is not overly influenced by very small-scale variations of the surficial salt distribution. In the lab, this depth captures the entire samples. The application time of 1 h is also favoured in other papers [10]. (2) An application for 24 h was discarded for practical reasons as the drying poultices can fall down, be rained on, or damaged by passers-by. Anyway, it is obviously necessary to keep the application time constant during an investigation.

Drill dust

The conductivity values (μs cm^{-1}) shown in Fig. 5 relate to the immersed drill dust from different depth intervals (0–0.5 cm to 1.5–2 cm), obtained from a stone cube soaked in $NaCl/Na_2SO_4$ solution of 0.5 mol l^{-1}. As with the PPP, drill sampling was carried out at different saturation levels. Under saturated conditions as well as in dry, salt-unloaded stone, conductivities are relatively uniform at the different drilling depths. At intermediate saturation (10, 50, 75%), the range between the saline solutions collected close to the stone surface and those from deeper drilling levels is remarkable, with salts being concentrated in the outermost 0.5 cm near the surface. The biggest gradient in conductivity decrease happens from the surface layer (0–0.5 cm) to the deeper subsurface (0.5–1 cm). The lower absolute salt content at lower saturation is probably due to salt efflorescence at the surface of the stone blocks (approx. 1 g within 120 h).

Conductivity versus salt concentration

Selected samples were analysed by Ion Chromatography to receive the mass concentration (mg cm^{-3}) of the saline solution. The results correlate very well ($R^2 = 0.98$) with the conductivity (μs cm^{-1}) measured by the conductivity sensor. This means that cheaper conductivity measurements can be applied without losing significant accuracy, and the measured values can be converted into salt concentration using a calibration function (plotted in Fig. 6). In the concentration range covered by our measurements (up to 1 mol l^{-1}) the conductivity (μs cm^{-1}) is directly proportional to the salt concentration. However, we have to bear in mind that conductivity also depends on e.g. the size of ions and the amount of charge carriers of the ion [25], so that a different calibration curve applies when the ion composition is changed.

Field investigation

Paper pulp poultices

The distribution of salt ions, sampled by poultices and measured via conductivity at the boundary wall of the fellow garden of Worcester College, shows obvious correlation to the weathering phenomena occuring at the stone masonry. Figure 7 shows the spatial distribution of the salt ions at the east-orientated wall side facing to the fellow garden. The PPP conductivity measurements illustrate higher values at wall parts with certain weathering phenomena than at parts with intact, unweathered stone surfaces. The highest conductivity values are detected at sampling points with cavernous weathering (Fig. 7).

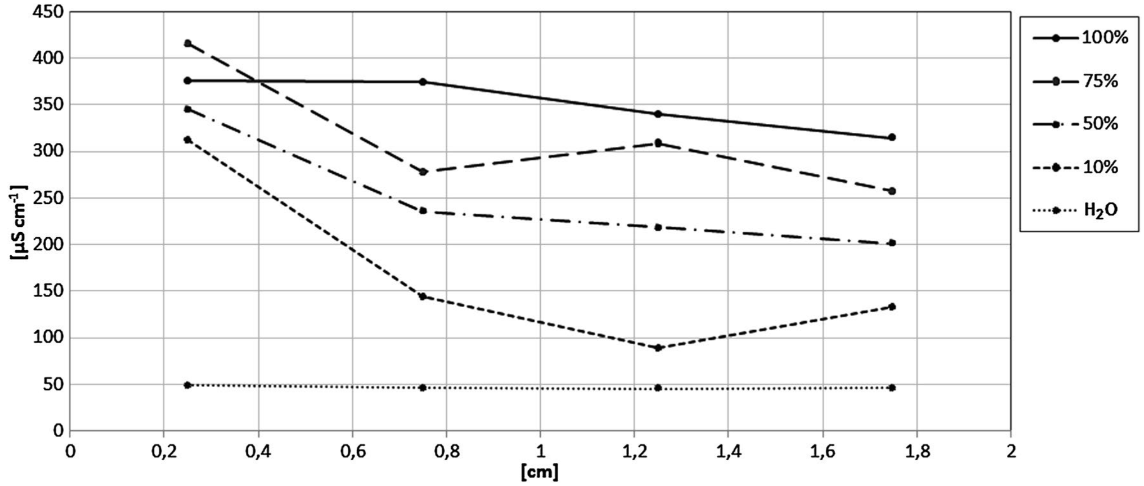

Fig. 5 Conductivity (μs cm^{-1}) of different saturation levels at various depths (0–2 cm)

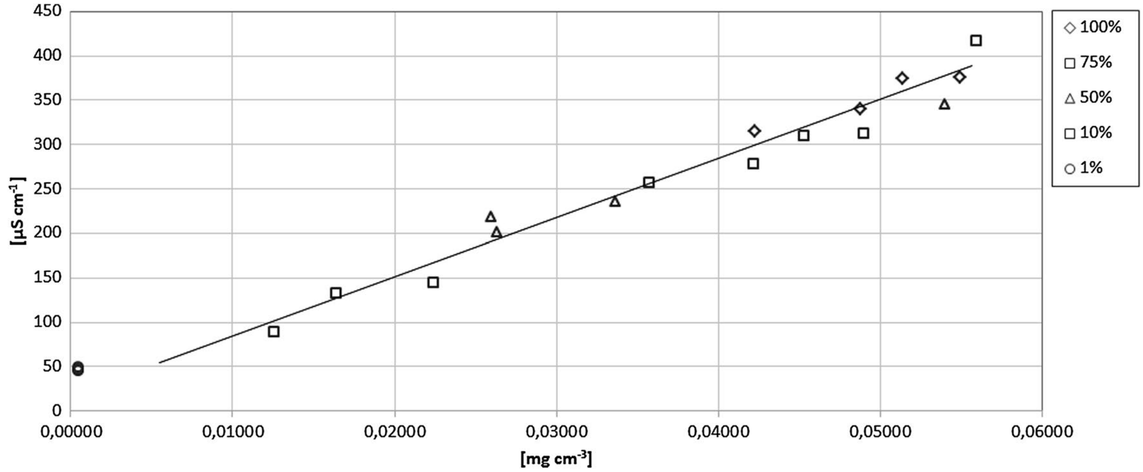

Fig. 6 Conductivity (µs cm^{-1}) vs. mass concentration (mg cm^{-3}) of different samples; coding shows different degrees of saturation

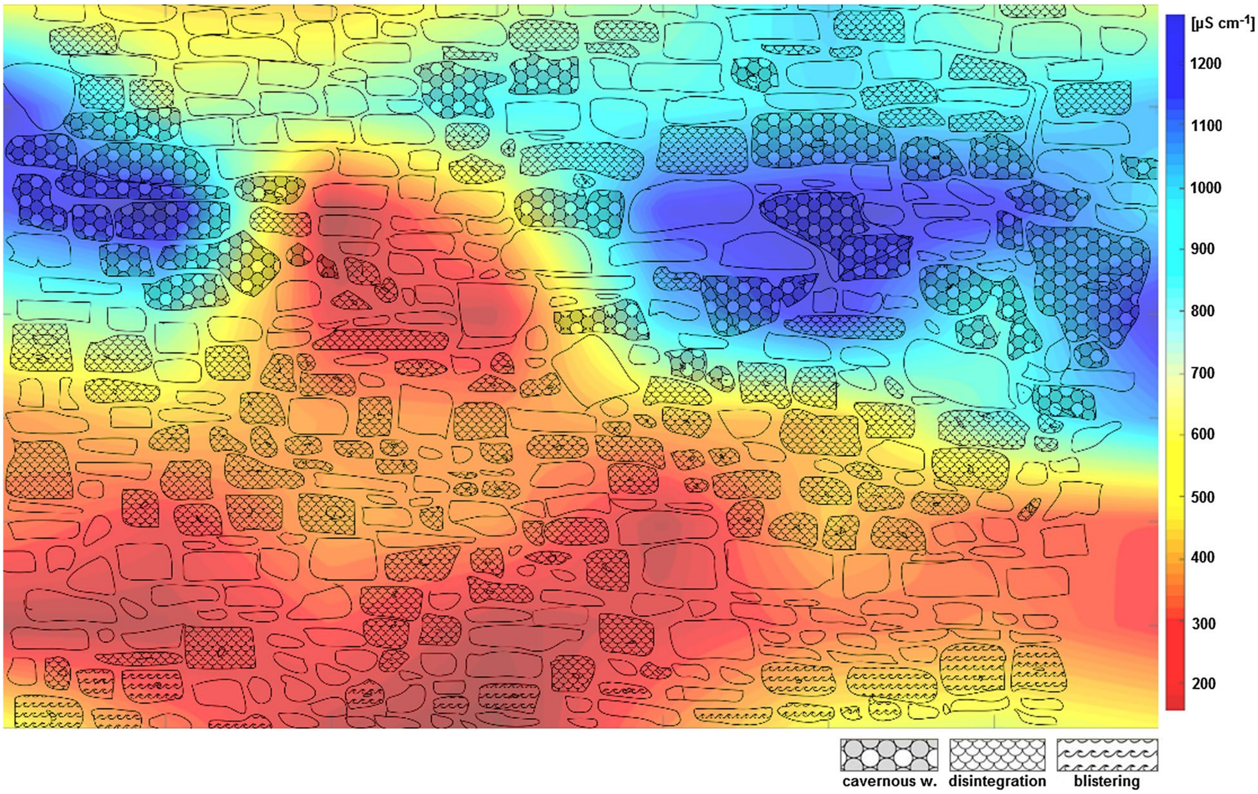

Fig. 7 Distribution of salt ions at the garden-orientated boundary wall of the college measured via conductivity (*red colours* low salt contents; *blue colours* high salt contents)

The PPP ion concentrations at the boundary wall are illustrated in Fig. 8 (left side). At the weathered zones of the masonry, higher concentrations of anions were detected than at parts with intact, unweathered stone surfaces. Hightened values of chlorides were found in areas with black crusts or disintegration while areas with cavernous weathering and blistering show lower values. Increased sulfate concentrations were detected at all weathering features. Taking into account the higer molar weight of SO_4^{2-} compared to Cl^-, chlorides seem to be more mobile and tend to moves quicker from the substrate into the PPP. At intact surfaces, blistering and cavernous weathering, little or no chlorides seem to be abundant. The solubility of sulfate depends on the salt type. Gypsum ($CaSO_4$) is a hardly soluble salt while other sulfates shows different levels of solubility, e.g. for Na_2SO_4, the solubility depends on temperature and relatively humidity [26–28].

Furthermore, Fig. 8 (right side) displays the PPP concentrations of the lab experiment in comparision to the field work. The PPP concentrations from the lab experiment were recalculated, because the applied poultices were 25% smaller than the poultices applied at the boundary wall. The stone cubes in the lab were initially soaked with a solution of 0.5 mol l^{-1} of NaCl and Na_2SO_4 and one time with H_2O, as base level. The displayed lab PPP concentrations reflect different saturation levels (0–100%) of the samples. The concentrations pertaining to different saturation degrees are in a narrower range for chlorides and reflect much more lesser PPP concentrations than for sulfates. This spread between chlorides and sulfates is due to the mentioned difference in molecular weight between NaCl (58.44 g mol^{-1}) and Na_2SO_4 (142.04 g mol^{-1}). With this background knowledge it is possible to approximate the concentration of the original amount of salt solution (mol l^{-1}) inside the stone pore system of the boundary wall. Chlorides are mostly in the range between 50 and 300 mol l^{-1} and sulfates, apart from outliers, in the range of approximatly 50–600 mol l^{-1}. This corresponds well with the salt solution of 0.5 mol l^{-1} used in the lab, when a surficial saturation level of 25% is assumed. A saturation of 0% is highly unlikely, and 50% or higher saturation is also unlikely because there was no rainfall at the time of PPP application. Above-average PPP salt concentrations are probably due to a higher salt concentration of the pore water (c. 0.5–1 mol l^{-1}), provided that there are no significant differences in water content across the surface of the wall. In general, it is not possible to quantify to which degree the PPP concentration is influenced by the pore water concentration in the stone (mol l^{-1}) or by the saturation level (0–100%).

The results of the PPP conductivity at the boundary wall are generally similar to the PPP conductivity in the lab (Fig. 9). The range of results for the most prominent weathering features (soiling, disintegration, cavernous weathering) corresponds best with pore water concentrations of 1 mol l^{-1} and low to medium saturation levels which seems to be a reasonable assumption. The results would also correlate with much lower fluid concentration of e.g. 0.1–0.5 mol l^{-1} under high to fully saturated conditions which is, however, very unlikely at a vertical stone wall during dry weather. This ambiguity will be expanded on in the "Discussion" section. Intact surfaces display much lower PPP conductivities which correlate with rather low fluid concentrations (0–0.1 mol l^{-1}).

Stone surface material

At some weathering 'hot spots', high to very high salt concentrations were found in the samples of the poorly adhesive stone surface (Fig. 10, left side). The amount of sulfates is highest on average in areas of cavernous weathering, but the highest singular maximum was determined in the disintegrated area (4609 mg l^{-1}). The

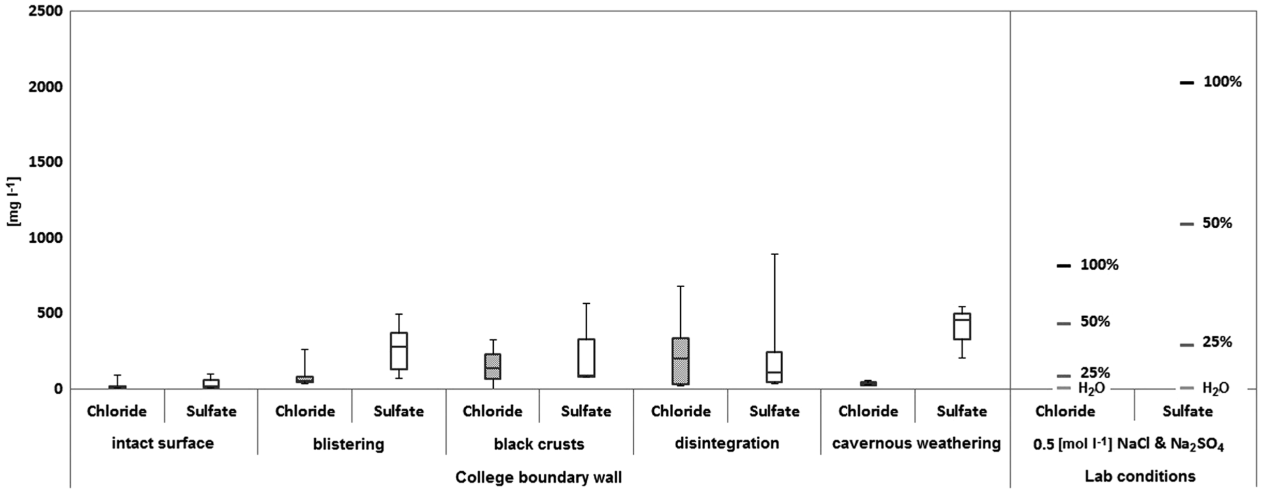

Fig. 8 *Left side* PPP concentrations (chloride and sulfate) at the college boundary wall (*box* reflects range between samples; maxima and minima as *error lines*); *right side* PPP concentrations (chloride and sulfate) of different saturation degrees of stone cubes (soaked with 0.5 mol l^{-1} saline solution and H_2O) under lab conditions. Note the higher molar weight of SO_4^{2-} compared to Cl

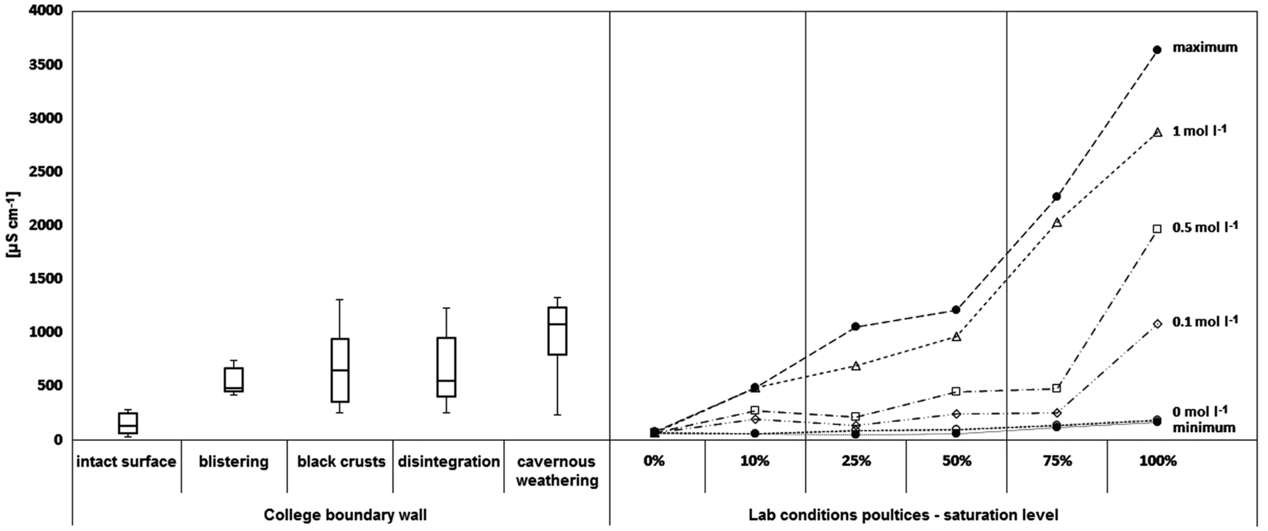

Fig. 9 *Left side* conductivity (µs cm^{-1}) of the saline solutions collected by poultices at the college boundary wall (*box* reflects range between samples; maxima and minima as *error lines*); *right side*: conductivity (µs cm^{-1}) of different concentrations of a saline solution under different saturation degrees collected by poultices under lab conditions (*vertical green* dividing lines imply the probable saturation range at the field site)

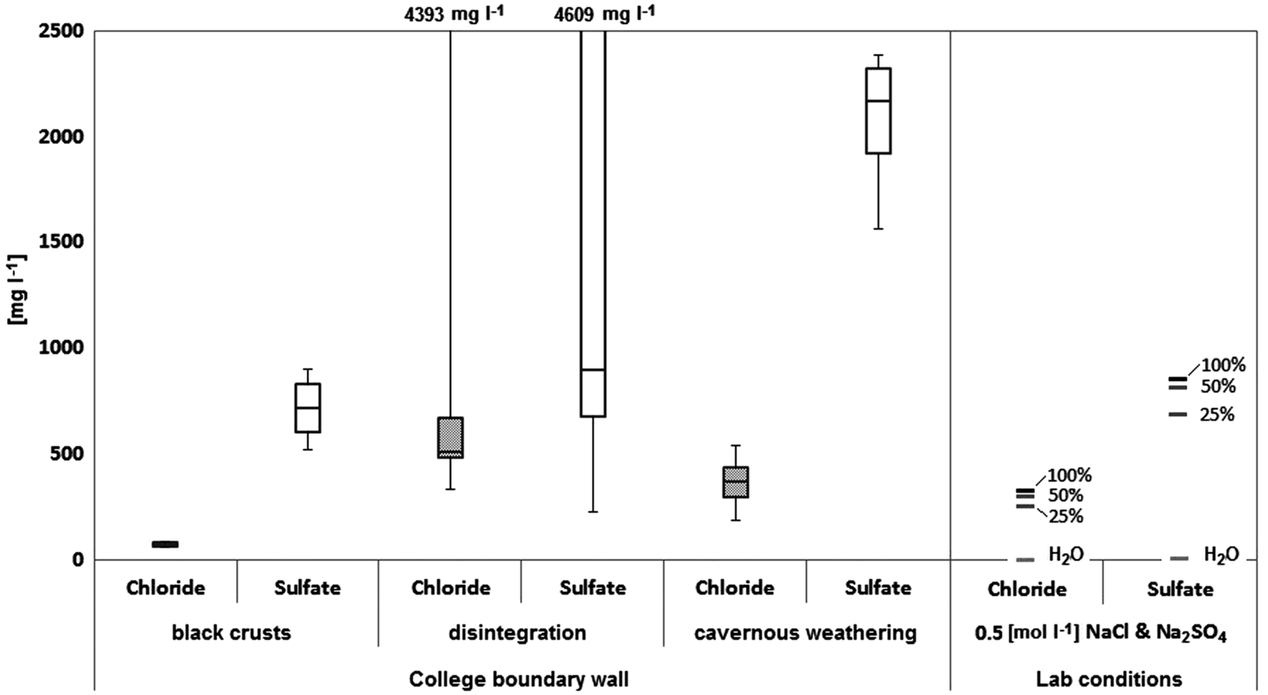

Fig. 10 *Left side* chloride and sulfate concentration of poorly adhesive stone material of the boundary wall (*box* reflects range between samples; maxima and minima as *error lines*); *right side* anion concentration of the drilling dust sampled (0–1 cm depth) and H_2O under lab conditions (*bars* show different saturation degree and H_2O)

lowest amounts of sulfates were detected on the intact stone surfaces. The concentrations of chlorides are generally lower, except of a singular very high maximum (4393 mg l^{-1}) in the area of disintegration. Taking the molar weight into account, chlorides seem to be particularly important in the disintegration areas and less important for cavernous weathering which matches the results of the PPP sampling. The drilling dust sampled

Table 1 Original pore water concentration in the lab and related PPP conductivity

Salt concentration	Original salt solution	PPP conductivity, 100% saturated		PPP conductivity, 75% saturated		PPP conductivity, 50% saturated		PPP conductivity, 25% saturated		PPP conductivity, 10% saturated	
mol l^{-1}	µs cm^{-1}	µs cm^{-1}	%	µs cm^{-1}	%	µs cm^{-1}	%	µs cm^{-1}	%	µs cm^{-1}	%
1	15,345	2200	14	1570	10	651	4	491	3	371	2
0.5	7673	1500	20	317	4	160	2	341	4	279	4
0.1	1535	830	54	196	13	181	12	146	10	98	6

from stone cubes (soaked with 0.5 mol l^{-1} NaCl and Na_2SO_4) during the lab experiment shows (for the outermost 0–1 cm) similar values as the surface material of the weathering zone of the wall. The sulfate concentrations in the areas of black crusts agree with the sulfate values of the lab analysis while in the disintegration and cavernous weathering zones the values are much higher. It has to be considered that the collected stone surface material belongs to the outermost 0.5–1 cm of the wall and that the salt ions might be concentrated near the surface. In comparison with the lab experiment (Fig. 9, right side), the area of weathering features like disintegration and cavernous weathering probably have a much higher salt concentration (up to 1 mol l^{-1} or more). Other than with the salt extraction by PPP, the degree of water saturation of the stone has much less impact on the results of drilling and sampling (cf. Figs. 8 versus 10).

Discussion

Salt solution behaviour during the dehydration process

The most significant result of both sampling methods is that the conductivity (μS cm^{-1}) increases with rising saturation levels. The highest PPP and drill dust conductivity was measured at c. 100% saturation, but the area with the strongest gradients differs between the methods. The conductivities of the PPP samples strongly decrease between 100 and 50% saturation, following then by a slightly falling curve down to 0% saturation of the stone cubes. This progression may emerge because salt ions are much better mobilised in an almost fully saturated stone than under partially saturated conditions. The poultices insert water into the stone, which enables capillary transport to a certain depth. Stones with a poorly interconnected pore system attain lower saturation because a lot of large air-filled pores remain [11, 14]. Stones with well interconnected pores are able to reach a higher saturation degree, so the range of the transport induced by the poultice may reach deeper regions of the stone and more salt ions can be activated.

The same apparent decrease of salt contents with decreasing saturation level is found in the drill samples. This is surprising and not readily understandable as all samples were treated with the same amounts of saline solution; thus, the absolute amount of salts should be independent from the water content of the sample. This phenomenon can be explained be significant surficial efflorescence during the drying process. These salt crystals were scratched from the surface before drilling which explains the apparent mass loss (in future work, this problem might be solved by accurate weighing and analysis of the removed material, which was neglected). In the drilling dust, the strongest decrease in ion content is found at the lowest saturation levels. From about 25% downwards the conductivity of all sample curves are strongly declining. The same result was obtained by the IC (mg l^{-1}). From the drilling profiles we can see that the amount of salt ions is almost uniform at low saturation degrees. These results are in contrast to intermediate saturation, where a well visible (decreasing) gradient between the stone surface and all deeper locations occurs. This result further underpins that salt ions favourably crystallise near the surface in the course of the dehydration process (e.g. [29]; however, a certain minimum moisture content needs to be maintained for an effective salt transport towards the surface.

Effectivity of salt sampling by PPP

Two basic questions of PPP sampling are: (1) how much salt ions can a poultice extract compared to the total amount of salt ions inside the stone? and (2) how deep does the influence of the poultice reach during its application to attract salt ions? To answer the first question, salt concentrations of the PPP samples and the drilling samples were correlated. Because of the different mode of sampling the absolute conductivity values are different; the saline solutions obtained by immersion of the poultices reach much higher values (up to 2800 µs cm^{-1}) than those of the drill dust (up to 430 µs cm$^{-1)}$. The poultices have a contact area to the stone surface of approx. 13.7 cm^2 while the stone powder derives from a drilling area of c. 0.79 cm^2. Thus, the absolute amount of available salt ions is much higher for the PPP method. To correct for this difference, the drilling results were corrected by area to make them comparable to the PPP sample.

One stone cube can take up approximately 50 ml of saline solution. The results of the drilling samples were extrapolated to the entire stone cube. The resulting amounts of salts, which are present in the stone cube match quite well the total amount of salts deriving from the initial saline solution (deviation of 4–15%). These values were compared to the amounts of salt extracted by the respective poultices. The result is that the amount of salt a poultice is able to take up depends on the saturation of the stone cube. Approximately 24% of the salts within a 100% saturated stone cube moved into the poultice within the 1 h of application. At 75% and lower saturation degrees, only 11–14% of the salts moved into the respective poultices. For the field setting, the amount of anions extracted by PPP was 6–63% (mean 20.7%) of the amount found in the stone samples. While the mean is broadly comparable to the lab results, the wide range of values renders it questionable to establish any rule-of-thumb. The remarkable difference between sampling by PPP and sampling via stone surface material highlights that the poultices are not able to take up the whole amount of salt ions available in the stone material. Thus, the effectivity of the poultices depends also on the solubility of the salts as well as on the depth of salt extraction [18].

Furthermore, we compared the conductivity of each prepared concentration of the original $NaCl/Na_2SO_4$ solution to the PPP conductivity under different saturation conditions (Table 1). This ratio increases with decreasing salt concentrations and decreases under lower saturation levels. Accordingly, the amount of extractable salts by PPP depends on the concentration of salt ions in the pore water as well as on the absolute amount of salt ions in the pore system. For practical application, this means that the back-calculation of pore water concentration from PPP results is difficult because of two unknown variables in the equation.

We assume a state of saturation between 25 and 50% for the surficial some cm of the boundary wall stone at the time of sampling. This assumption is backed e.g. by simulation results from building physics that consistently show higher pore water levels inside a wall and strongly decreasing saturation towards the surface [30, 31]. Near the surface, moisture levels strongly fluctuate in reaction to changing weather conditions [32] and as we sampled in a phase of rather dry weather, rather low saturation appears to be highly probable. Under the reasonable assumption of 50% saturation, the PPP concentrations would have to be multiplied by the factor 8–25 to calculate pore water concentration (cf. Table 1). When higher or lower saturation levels are considered, the range of possible multiplicators is even larger. This means that the PPP method can provide semi-quantitative information on salt distribution, but no absolute amounts. In future work it would be beneficial to obtain additional information on the pore size distribution of the samples.

Depth of salt extraction by PPP

The depth to which salts are extracted by PPP depends upon capillarity and upon the duration of PPP application. As shown in Fig. 4, shorter (10 min) or longer application (24 h) lead to higher PPP concentrations than the used 1 h interval and might, thus, be preferable for desalinisation purposes. For analytical purposes as in our approach, we advocate the 1 h interval because the calculated (rather theoretical) penetration depth of approx. 6 cm provides a reasonable integration over the outermost stone layer while the 10 min interval captures 2.5 cm depth at maximum. Of course, application time should be chosen according to the target depth of the investigation. Near-surface salt accumulation at stone (sub)surfaces is variable in time and space, but tends to be concentrated in the outermost stone layers (e.g. [33, 34]). Desalination projects illustrated that also after an in situ surface application by poultices salts tend to accumulate at a certain depth [11]. This is probably due to the migration of salts not only towards the surface, but also to internal drying interfaces.

Relation of salt distribution to weathering phenomena

Wall parts with intact, non-weathered stone surface are characterised by very low anion concentrations, although few points show PPP concentrations up to almost 100 mg l^{-1}. Weathered areas with features like disintegration and crumbling show the highest amount of salt ions, following by black crusts and blistering. Salt ions obviously accumulate and crystallise in these zones. Similar patterns were found in the field by Turkington and Smith [34] and Martinho et al. [10]. Salt deposits and efflorescence are visible at and close to these weathering spots. Upwards and downwards of the cavernous weathering zone the surface of some stone blocks shows strong disintegration. These spots seems to be 'juvenile stages' of cavernous weathering, because the main part of the respective block surfaces seem to retreat the faster, the closer they are located to the main cavernous weathering zone. These areas of strong disintegration show up to two times higher salt ion values than in the cavernous weathering zone itself. In view of development of cavernous structures, it has been demonstrated that the frequency of caverns increases as weathering proceeds in the early stages [34]. While the high amount of salt ions is a probable reason for the development from disintegration zones to zones of cavernous weathering, the reason for the relatively lower salt content in the cavernous zone is not fully understood. Inhomogenities in the stone fabric, which often lead to aveolar weathering are not visible at the blocks of the investigated masonry. Reasons for the development of cavernous patterns might also be a different behaviour and interaction of highly soluble and poorly soluble salts [29, 35, 36] or a concequence of mechanical breakdown of stone surfaces exposed after crust removal [37]. Furthermore, salt concentrations are highest in the area of the capillary fringe, and they are much higher on the garden side of the wall, which is surprising because the starting hypothesis was that road salts and air pollution should be rather concentrated on the road side. We assume that the road side receives higher amounts of driving rain, washing down salts from the surface, and that saline solutions migrate towards the drier garden side.

The samples from some weathering features of the college wall (e.g. black crusts) are within the spectrum of the lab results with 0.5 mol l^{-1} salt solution, while others (disintegration and cavernous weathering) show considerably higher values, suggesting that at these spots a much higher concentration of salt ions than 0.5 mol l^{-1} is present in the stone (sub-) surface.

Conclusion

As a summary and for practical application, we conclude that PPP are well suited to outline the spatial distribution of harmful salts at a masonry surface and assign them to certain weathering features if attention is paid to a standardised procedure (e.g. uniform duration of application). Due to the concurrent influence of pore saturation and salt concentration, quantitative information is still difficult. A larger body of data from different settings and working groups might help to overcome this problem.

Authors' contributions

Conception or design of the work: IE, OS; Data collection: IE; Data analysis and interpretation: IE, OS; Drafting the article: IE; Critical revision of the article: IE, OS; Final approval of the version to be published: IE, OS. Both authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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