

# NaCl-Related Weathering of Stone: The Importance of Kinetics and Salt Mixtures in Environmental Risk Assessment

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## Research article

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# Abstract

Salt weathering is one of the most important causes of deterioration in the built environment. Two crucial aspects need further investigation to understand the processes and find suitable measures: the impact of different climatic environments and the properties of salt mixture crystallization. We demonstrate the importance of kinetics in quantifying crystallization and dissolution cycles by combining droplet and capillary laboratory experiments with climate data analysis. The results proved that dissolution times for pure NaCl were much slower than crystallization, while thermodynamic modelling showed a lower  $RH_{eq}$  of NaCl (65.5%) in a salt mixture (commonly found in the built heritage) compared to its  $RH_{eq}$  as a single salt (75.5%). Following the results, a minimum time of 0.5 hour is considered for dissolution and the two main  $RH_{eq}$  thresholds could be applied to climate data analysis. The predicted number of dissolution/crystallization cycles was significantly dependent on the measurement frequency (or equivalent averaging period) of the climatic data. An analysis of corresponding rural and urban climate demonstrated the impact of spatial phenomena (such as the urban heat island) on the predicted frequency cycles. The findings are fundamental to improve appropriate timescale windows and to illustrate a methodology with specific points of interest to quantify salt crystallization cycles in realistic environments as a risk assessment procedure that can be applied to climate data. The results are the basis for future work to improve the accuracy of salt risk assessment by including the kinetics of salt mixtures. This will improve the understanding of past and future salt weathering mechanisms and enable scientifically informed conservation strategies.

## 1. Introduction

As a result of a UK-Belgium network project (1) and introduction to a joint PhD project (2) to tackle the challenges that face built heritage in a rapidly changing society and climate, salts and consequential weathering were considered understudied and vital to establish proper conservation management strategies. Understanding crystallization phenomena is essential for a range of different disciplines from geological systems, industrial processes to the built environment. A wide range of literature is available considering the effects of salt crystallization in porous media, broadly defined as salt weathering with several important texts on the impact on natural stone materials such as the milestone references on natural landscape formation by Goudie and Viles (3) and the review by Evans (4). In contrast, the literature about stone in the built environment has focused on practical approaches to addressing stone conservation (e.g., (5–8)). Fundamental questions, such as the mechanisms of crystallization and the development of crystallization pressure in porous media, remain open questions and active areas of research (e.g., (9–19)).

To understand salt crystallization processes and develop sustainable risk assessment methodologies, scientists rely on experimental testing and theoretical models to predict the behavior of salts. Several experimental tests have been designed, debated and drafted in standard procedures, as is currently being done by the RILEM Technical Committee 271 ASC (11). In theoretical models the critical relative humidity thresholds are determined as a method to predict if a single salt will undergo a phase change in certain environmental conditions, as described by e.g. Sabbioni *et al.* (20). However, thermodynamic calculations are, simply stated, based on ionic activities and thus consider ideal solutions, which allow error in realistic conditions. Additionally, the deliquescence points of salt mixtures cannot be directly determined from those of the single salt components in the mixture, so they must be calculated, as described by Steiger *et al.* (21). To determine the critical crystallization points for salt mixtures the ECOS/RUNSALT model (22,23) is the only available model capable of predicting the behavior of salt mixtures under changing climate conditions. The system is based on the thermodynamic approach of Pitzer (based on mole-fractions rather than molalities) and represents a major achievement, enabling the prediction of the equilibrium behavior of salt mixtures. However, the kinetics of salts are not considered, and the model has several limitations. The constraints in which the results of such a model should be interpreted are rarely published (24). Furthermore, fundamental research on salt mixtures can only be found in recent literature and is rare, e.g. (25–28).

The dependency of salt phase transitions on temperature and relative humidity, illustrated by the ECOS/RUNSALT outputs, underpin climatic control to mitigate salt damage. Therefore, this environmental risk has frequently been assessed by testing meteorological observations to parameterized relevant phase transitions. Grossi *et al.* (29) and Sabbioni *et al.* (20) have used

thresholds of 75.3% RH and 75.5% respectively, as indicators for sodium chloride (NaCl) crystallization-dissolution cycles, testing average daily relative humidity from meteorological observations and taking negative crossings (crystallization) as a proxy for crystallization-dissolution cycles. Establishing a correlation between daily observations and monthly averages for a certain climate allowed them to link the environmental risk to different climate and climate projections. Benavente *et al.* (30) used a similar single threshold approach of daily averages for NaCl phase transitions for a case study on the Postumius Tomb (Spain), but considered a critical relative humidity difference of 10% for NaCl, setting the RH threshold at 65.3% for two consecutive days. This single-threshold approach can be justified as the non-hydrating NaCl  $RH_{eq}$  has a low temperature-dependent variation. Both Grossi *et al.* (29) and Benavente *et al.* (30) have used a more complex, temperature-dependent indicator for the hydrating sodium sulfates. Godts *et al.* (24) counted phase transitions of complex salt mixtures based on thresholds of the ECOS/RUNSALT outputs for a fixed temperature, using six- and twelve-hourly RH variations in the case of the St. James Church (Liège, Belgium). Menéndez (31,32) used a similar approach, estimating damage based on salt volumes changes calculated from ECOS/RUNSALT models. The output has been compared to relative humidity changes assuming constant temperature of daily meteorological data of several locations in France.

In response, this paper presents the results of an investigation on salt weathering assessment methodology that considers the temporal and kinetic behavior of salts present in porous media, in urban or rural environments. To illustrate the methodology, we consider an ideal situation with pure unconfined and confined NaCl directly influenced by changing RH's and NaCl in a mixture. The dissolution and crystallization rates of NaCl under realistic changing climatic conditions are investigated. This in turn is the basis for continuing research [2] to identify phase transitions of salts in a mixture and predict the damage potential in changing climatic conditions, past and future. The aim of this paper is to identify the limitations of current approaches, the challenges to better risk assessment, and the future work required to enable them or address these (e.g. laboratory work). Specifically, this paper wants to guide future development of sustainable conservation and risk management strategies in order to mitigate the harmful impacts of salts.

## 2. Experimental Methodology

### 2.1. Dissolution and crystallization properties of NaCl - Droplet experiment

For the purpose of this methodological study the dissolution and crystallization times of a NaCl crystal/solution are considered (Fig. 1). The obtained values are determined via time lapse videos (5 sec. resolution) (3D-digital microscopy, HIROX) by recording the solution/crystal under changing RH in a microclimate chamber (GenRH/Mcell, N<sub>2</sub> gas flow: 200 sccm). A NaCl crystal (80 ± 10 µg) (EMSURE® Merck, NaCl for analysis 1.06404.0500) is placed in the chamber (Mcell) on a carbon adhesive tape. Twelve steps of RH changes are carried out at a temperature of approximately 20 °C. Each step considers a start and a target RH. For instance, the dissolved crystal (diluted salt solution) is conditioned at 90% RH (start RH) (respective concentration: 2.85 mol.kg<sup>-1</sup> and droplet diameter: 409 µm), followed by a decrease to 70% (target RH).

When complete crystallization is noticed, the RH is increased back to 90% until complete dissolution. The experiment continues by subsequently decreasing the target RH in steps of 10% to a minimum of 20%. The initial decrease is 20% from 90 to 70%, which is below the  $RH_{eq}$  of the NaCl. This is followed by an increase to 90% and again a decrease to 60% and so forth. The crystallization time starts at microscopic visual crystallization, that is, when the crystal(s) appear(s) to grow, and ends when growth is no longer visible, thus when the supersaturated solution film at the interface crystal/surface is no longer observed under the microscope. For the dissolution rate we consider the moment when wetting of the crystal becomes visible, followed by complete dissolution of the crystal(s). The target RH's in the equipment are reached between 3 and 11 minutes for respectively the RH targets from 90 to 20 and 90 to 70%, while 6 to 3 minutes are recorded to reach 90% starting at respectively 20 and 70%.

### 2.2. Dissolution and crystallization properties of NaCl - Capillary experiment

Additionally, the dissolution and crystallization times of NaCl were investigated in round glass capillaries (id: 100  $\mu\text{m}$ ). A NaCl solution ( $4 \text{ mol.kg}^{-1}$ ) is introduced into the capillaries in varying volumes and depths (see results) and is left to crystallize in four separate capillaries under lab conditions (approx. 60% RH and  $\approx 21 \pm 1 \text{ }^{\circ}\text{C}$ ). Four capillaries are chosen to represent the influence of different volumes and depths. Afterwards the samples were conditioned at 90% RH and  $20 \text{ }^{\circ}\text{C}$  until the solution stops expanding as shown in Fig. 2, which is when the solution concentration reaches  $2.85 \text{ mol.kg}^{-1}$  (the equilibrium concentration at 90% RH). The dissolution and crystallization times of NaCl were investigated with the same method as described above for the droplet, limited to one RH step from 90 to 20%; and vice versa to 90% RH.

The total length of the solution and distance from the capillary entrance(s) to the solution (inner sides of meniscus) is measured before lowering the RH. Both measurements are taken to respectively calculate the solution volume and consider the influence of the depth of the solution on the crystallization time. The volume of the solution in the capillary is calculated based on equations 5 and 6 in Shen *et al.* (2020). Unlike Shen *et al.* we do not present results on the supersaturation at the onset of crystallization, but the total time of completed crystallization/dissolution with respect to the distance from the capillary entrance of the solution in the capillary.

## 2.3. NaCl in a salt mixture - Thermodynamic modelling with ECOS/RUNSALT

To illustrate the effect of the presence of other salts on the  $\text{RH}_{\text{eq}}$  of NaCl, the crystallization behavior of the single salt and a realistic complex mixture were modelled using ECOS/RUNSALT freeware (22)(23). The mixture represents a commonly found solution in deteriorating building materials in Belgium. Ion chromatography results derived from a drill sample taken at a height of 25 cm and to a depth of 2 cm from a deteriorating limestone (in the Cathedral of Antwerp, Belgium) are used as input for the model. Specific information concerning the limitations and input method of the model are described in Godts *et al.* (24). The output is modified from the original to represent non-cumulative amounts. When using the model, equimolar contents of calcium and sulfate ions, considered as the gypsum content, are excluded. Also, an excess of calcium ions is excluded which is associated with a small amount of calcium carbonates dissolved during the extraction process in ultra-pure water.

## 2.4. Predicting the occurrence of dissolution cycles - Meteorological data resolution (spatial and temporal)

To study the impact of data properties when using climate data to estimate the occurrence and risk of salt crystallization cycles, a threshold-based indicator is applied to two high-time-resolution datasets representing urban and rural climates. The urban and rural climates are represented by measurements at two locations. A typical 'urban' climate is represented by climate monitoring in central Ghent, a mid-sized city in the west of Flanders, Belgium. The corresponding 'rural' climate is represented by the climate monitored in Melle, a region several miles outside of Ghent without significant anthropogenic impacts on the local environment. The data was originally collected as part of a project to produce high-quality climate monitoring of several areas within the urban area of Ghent (33). The local environment is monitored at a 1-minute frequency.

The indicator represents the predicted number of instances in which dissolution would likely occur by comparing average RH% between subsequent periods of time. To evaluate the importance of data resolution on the estimated number of dissolution/crystallization cycles, an 'averaging window' of several difference widths, ranging from 1 minute (the data frequency) to 24 hours (used previously in humidity fluctuation calculations by Arfvidsson (34)) was considered. The averaging window is an analogue for climate data recorded at wider time intervals, although these can be recorded as either individual measurements taken at regular intervals or the average of several measurements taken within that time period. Thus, the importance of the data frequency is a crucial factor to consider as shown by Wilhelm *et al.* (35) when considering frost events causing catastrophic decay of limestone. Similar events concerning salt crystallization can be missed if the resolution of the data is too coarse or certain environmental factors are not considered such as rainfall, wind velocity, surface condensation and direct sunshine. For example, when dissolution happens after rainfall, the solution might be undersaturated

and the necessary time before supersaturation is reached is likely to take more time. Even though the influence of above mentioned environmental factors are not taken into consideration in this study, it is likely that the crystallization time will remain significantly below the dissolution time, also for undersaturated solutions.

Two thresholds are considered in this paper:

- 75.5%, representing NaCl present as a single salt
- 65.5%, representing the behavior of a salt mixture that includes NaCl

Previous work has used a single threshold of 75.3% to study phase transitions (29). However, herein a threshold of 75.5% is considered, based on the water activity ( $a_w$ ) of NaCl determined for a range of ambient temperatures. Although the temperature in both locations varies over the course of the year, the mean temperatures at the urban and rural sites were 12.5 °C and 11.5 °C, respectively. Based on the precision of the measured temperature data, these correspond most closely with  $a_w = 0.755$  (at 10 °C for a saturated sodium chloride solution 6.135 mol.kg<sup>-1</sup>). It also remains important to keep in mind that crystallization is affected by a range of different factors (see (19)) and dissolution of salt crystals takes more time compared to crystallization. Furthermore, a threshold of 65.5% RH is considered as the  $RH_{eq}$  of NaCl tends to shift in a mixture with other ions, thus representing a more realistic situation.

### 3. Results And Discussion

#### 3.1. Dissolution and crystallization times of NaCl - Droplet experiment

The dissolution and crystallization times of an unconfined NaCl droplet are illustrated in Fig. 3. As expected, NaCl crystallization is faster compared to dissolution and a correlation is found between RH ranges and dissolution/crystallization times. The wider the RH gap the faster the phase transition occurs. However, crystallization and dissolution do not have the same behavior, both rates decrease when the RH range increases, but not in the same proportion. Crystallization times follow a power approximation while dissolution follow a more linear behavior. Similar results were found in Desarnaud *et al.* (36). They studied the nucleation and dissolution rates of NaCl crystals from 0.1 µl droplets of a saturated NaCl-solution (6.16 mol.kg<sup>-1</sup>). The phase transition of NaCl crystals were observed from 50–100% and vice versa at a controlled temperature of 21 ± 1 °C. They observed that, at 50% RH the total time of NaCl-crystallization in a droplet of 0.1 µl on a hydrophilic surface is 5 min (± 0.1), while the total deliquescence time for the crystallized salt (0.36 mg) at 100% RH is two times longer (10 ± 2 min).

#### 3.2. Dissolution and crystallization times of NaCl - Capillary experiment

The dissolution and crystallization times of confined NaCl solution/crystal(s) at respectively 90% and 20% RH ( $\approx 21 \pm 1$  °C) are presented in Table 1 ( $D$  and  $C$ ). At the onset of the experiments, when dissolution is initiated, the crystal(s) are closer to the entrance of the capillaries ( $d1$ ) compared to distance of the solution meniscus to the entrance of the capillaries after completed dissolution (at 90% RH) ( $d2$ ). To clarify this, the experiments starts with the crystals in capillary 2 located directly at the entrance, thus 0 µm ( $d1$ ). The crystals are also partly positioned on the outer edge of the capillary (during dissolution the crystals dissolve and the solution is pulled inside due to capillary forces ( $d2$ ). Afterwards when crystallization is completed the crystal(s) are located further into the capillary. Logically the distance of the crystals from the entrance of the capillaries will influence the time at which water vapor reaches the crystal(s) and thus effects the dissolution time. The time is further influenced by the amount of salt that needs to dissolve and the available surface area of the crystal(s). These influencing factors are clearly illustrated as a correlation is distinguished between the time when crystals start to pick up water until the effective time for the crystals to (visibly) dissolve. For example, this time is appr. 22 and 24 min for capillaries 1 and 2, and more than 1 to almost 2 hours for capillaries 3 and 4 ( $D$ ). In contrast, completed dissolution (until the volume of the solution stops expanding after dissolution of the crystals at 90% RH) is appr. 59, 57, 35 and 20 min for the capillaries 1 to 4.

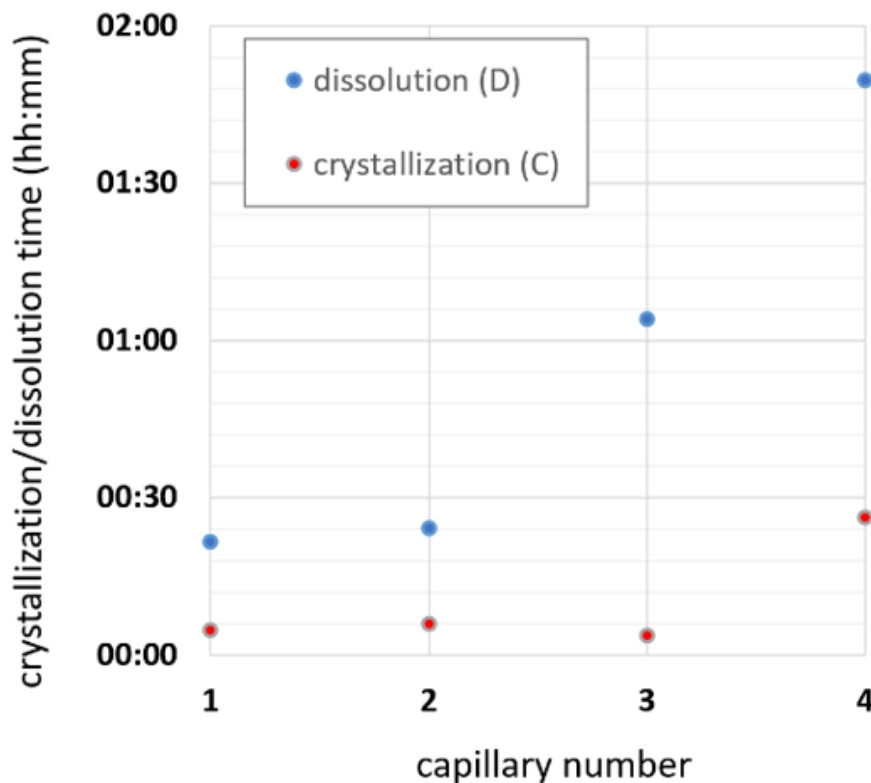
For the crystallization experiment each capillary contains a different volume of solution. The start volumes and distance of the solutions in the capillaries at 90% RH are shown in Table 1 ( $V1$  and  $d2$ ), at this point the solutions reached a concentration of  $2.85 \text{ mol.kg}^{-1}$ . When the equipment is set to 20% RH, after approximately 5, 7, 9 and 17 min ( $\pm 30$  s) (induction time) crystallization starts. Just before crystallization the solutions volumes ( $V2$ ) decreased to a minimum (reaching supersaturation). The distance ( $d3$ ) of the solutions from the entrance of the capillary increased compared to ( $d2$ ). The effective crystallization times ( $C$ ) are significantly below the dissolution times ( $D$ ). The sum of the induction time and the crystallization time ( $C$ ) equals the moment the equipment is set from 90 to 20% RH until completed crystallization. The total times are respectively 10, 13, 13 and 43 min ( $\pm 30$  s). The combined induction and crystallization time remains half the time for the crystals to visibly dissolve.

A solution with less volume deeper in the capillary can crystallize at the same rate as solutions with more volume near the surface, however dissolution times take longer at larger depths into the capillary and is less dependent on the volume of the solution. In Desarnaud *et al.* (2014) the same dependence of the distance of the solution from the capillary entrance has been found especially for the induction time. The complete dissolution time of a NaCl hopper crystal of  $2.31 \pm 0.1$  mg is  $34 \pm 5$  min, while the total crystallization time of the same amount of NaCl was twice as fast ( $17 \pm 3$  min), yet two times slower compared to droplet experiments. The results confirm the importance of focusing on dissolution rates rather than faster crystallization rates when counting crystallization/dissolution cycles in realistic environments.

Table 1

Dissolution and crystallization times (D and C) of confined NaCl crystal(s)/solution in 4 capillaries (id: 100  $\mu\text{m}$ ); also represented in the graph below as determined by (GenRH/MCell; Hirox) at different RH targets (90% for D and 20% for C). The distance ( $\mu\text{m}$ ) of the crystal(s)/solution to the entrance of the capillaries and the volumes of the solutions at different stages of the experiment are presented.

Capillary number (cap.)	Dissolution (90% RH) (hh:mm:ss)	Crystallization (20% RH) (hh:mm:ss)	Initial distance of crystal(s) from entrance of (c) at 20% RH ( $\mu\text{m}$ )	Distance of solution meniscus to the entrance of (cap.) at complete dissolution 90% RH ( $\mu\text{m}$ )	Distance from the entrance of (cap.) to the solution meniscus at the onset of crystallization ( $\mu\text{m}$ )	Start volume of the solution (complete dissolution at 90% RH) ( $\mu\text{L}$ )	Solution volume (onset of crystallization at 20% RH) ( $\mu\text{L}$ )
Code	D	C	d1	d2	d3	V1	V2
1	00:21:36	00:04:45	20	86	148	514	239
2	00:24:12	00:05:57	0	167	230	667	315
3	01:04:00	00:03:48	362	368	387	442	191
4	01:49:42	00:26:12	411	467	538	722	371



The approximation of crystallization cycles described further is significantly influenced by the location and the volume of the salt solution, comparable to salts either at the surface of a porous material or within the pores. Since dissolution takes more time, the approximation of the number of possible cycles (phase transitions) that can occur in a given environment should be based on the minimum dissolution times. Additionally, there are a wide range of factors that will further influence the results in realistic situations on site, such as:

- Pore- sizes, structure, filling (crystals/solution), impurities (pollution, dust, organisms, etc.)
- Depth (location) of the salt (solution) to the surface
- Orientation, water load (rain, rising damp, infiltrations, etc.), wind and sun exposure, and their respective rates of change

- Boundary conditions (building structure, materials, interfaces, past treatments, biological contamination, etc.)

At this point we considered an ideal situation with pure unconfined and confined NaCl directly influenced by changing RH's. Representing respectively a single salt at the surface of a stone and just below the surface in the first pores. However, one of the main influential factors is the presence of other ions in the solution. Accordingly, what follows includes a reflection on NaCl in a common salt mixture.

### 3.3. NaCl in a salt mixture - Thermodynamic modelling with ECOS/RUNSALT

To illustrate the experimental determination of crystallization cycles in realistic climatic conditions it is important to consider that single salts are rarely present in nature. On average a typical building material subjected to decades of water infiltration will contain a mixture of different ions, such as,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ . The salt content of a deteriorating limestone in the Cathedral of Our Lady in Antwerp is used to illustrate the influence of adding other ions to a binary system containing  $\text{Na}^+$  and  $\text{Cl}^-$ . Using the ECOS/RUNSALT model NaCl precipitates below the  $\text{RH}_{\text{eq}}$  of 75.3% at 20 °C (Fig. 4) and below the  $\text{RH}_{\text{eq}}$  of 75.5% at 10 °C. However, when the system contains other ions the  $\text{RH}_{\text{eq}}$  of NaCl changes. In the specific mixture presented (Fig. 5) NaCl will now precipitate below a RH of 65.5% at 20 °C. In the latter, the complexity of the mixture might also allow precipitation of double salts such as darapskite. The  $\text{RH}_{\text{eq}}$  of NaCl in a mixture will typically shift to a lower RH and is often seen in such outputs around  $\approx 65\%$ . Again, this shows the need to experimentally verify the behavior of salts in a mixture under changing climatic conditions.

### 3.4. Predicting the occurrence of dissolution cycles - Meteorological data resolution (spatial and temporal)

A threshold approach to analyze meteorological or climate data based on the  $\text{RH}_{\text{eq}}$  of salts has become an established method for testing the environmental risk related to salt damage. As mentioned in the introduction, most research uses daily averages of relative humidity, although some research takes advantage of multiple-hour averages. The pragmatic use of these time periods seems to relate to data availability. As pointed out by Camuffo (37), the frequency of observation should be related to the type of problem. In the case of salt phase transitions, this means taking into account its wicked kinetics influenced by a wide range of factors. Results of standard salt crystallization tests in unconfined (Fig. 3) and confined media (Table 1) for a single salt NaCl show a kinetic dependency on confinement, crystal size, ambient RH, RH oscillation, crystallinity, etc. This currently hinders an accurate time integration in an indicator based on a threshold approach. Nevertheless, these experiments show that dissolution is slower, hence being the limiting factor on crystallization-dissolution cycling, and that realistic time periods range from sub-hourly for unconfined droplets to multiple hours for confined droplets, thereby realistically occurring on a semi-diurnal scale. It should be noted that using meteorological data is only relevant for salt transitions near the surface of a stone, as the material itself buffers strong RH fluctuations at depth. As this is not easily defined for the stone's interior, hygrothermal models (also called heat-air-moisture models) could provide valuable input on RH gradients below the surface. It may even impact the conditions at the surface, emphasizing the need for microclimatic observations at the surface.

Grossi *et al.* (29) introduced the idea of salt climatology which implies a regional and seasonal dependency of the environmental risk of salt phase transitions. Additionally, it has been shown for other environmental risks such as freeze-thaw action that subregional phenomena such as the urban heat island (38) and microclimates around buildings, e.g., as the result of orientation (39), have a significant impact. The importance of both seasonality as well as local climate effects is also illustrated in this paper. Figure 6 presents the seasonal RH variations for the urban and rural meteorological data in and around Ghent (Belgium), using high-frequency meteorological observations of an urban environment in Ghent and its rural surroundings (data obtained from Caluwaerts *et al.* (33)). Grossi *et al.* (29) evidenced that more NaCl phase transitions are found when the monthly mean relative humidity is close to the 75% RH threshold. They found a sharp increase during spring months stabilizing in summer before declining in autumn, using meteorological data of weather stations in north western



France. Also, in the dataset presented in Fig. 6, seasonal averages are much closer to the transition point during spring and summer (for each of the indicator thresholds), suggesting a higher risk in these seasons. Even though extremes in winter and autumn cross the threshold, the averages are well above the threshold of both indicators, with an exception in the urban environment when considering the threshold of a NaCl as a single salt.

The average RH is generally lower in the urban environment compared to the rural environment. Using a 75.5% threshold, the average RH in the rural environment is closer to the threshold in spring and summer, whilst it is closer for the urban environment in autumn and winter, suggesting a higher risk in spring/summer in the rural environment and higher risk in autumn/winter in the urban environment. Using a 65.5% threshold, the risk is higher in the urban environment throughout the entire year, with all seasonal averages closest to the threshold. This illustrates the limitations of generalizations when studying the actual damage risk under different or predicted environments.

Additionally, there is also a dependency of the results on the averaging time window of measurement. Figure 7 shows the number of NaCl phase transitions using a 75.5 and 65.5% RH threshold, respectively based on  $RH_{eq}$  for pure NaCl and NaCl in a mixture, for different time windows of observation and environmental context. For time windows shorter than 10 minutes, the rural environment has a higher amount of fluctuations throughout all seasons which is not reflected in the datasets based on averages in Fig. 6. It is likely that high-frequency fluctuations (shown in Fig. 7) are buffered by the urban heat island effect. This is more pronounced in spring and summer, likely relating to short but extreme weather events occurring in those seasons (40). However, these high-frequency RH fluctuations possibly have less impact on salt crystallization due to slower kinetics of salt dissolution. A time window of 1 minute therefore illustrates an unrealistic high number of cycles, easily exceeding 200 cycles and sometimes almost approaching 800 per season, resulting in almost 2500 cycles per year. It's the result of short-term fluctuations around the 75.5 or 65.5% RH threshold, but not relevant for salt phase transitions that experimentally do not seem to occur on this timescale (Fig. 3 and Table 1).

There is a sharp decrease in number of cycles when enlarging the time window from one to 30 minutes. The trend between this quantitative approach and the qualitative evaluation of Fig. 6 is in agreement when discarding high-frequency data (< 20 min). When considering a time window of approximately 0.5 h, nearer to the dissolution time of droplets and smaller solution volumes in the capillaries presented herein (Fig. 3 and Table 1), the number of cycles is less than half compared to the maximum (at 1 min) for both urban and rural environments. There is a steady decrease in number of cycles between 0.5 h and 6 h. On the other hand, it can be observed that the number of cycles taken on a daily average (24 h) is well below the amount of these multiple-hour averages. Daily averages might underestimate the number of cycles if one would assume that phase transitions can occur in the range of a few hours as illustrated by the capillary experiments (Table 1). Whilst it is realistic to reject time windows below 0.5 h, the use of (semi-)hourly data versus (semi-)diurnal has a significant effect on the estimated number of cycles.

The trends observed in Fig. 6 are confirmed by the data of Fig. 7. The overall number of cycles is higher in spring and summer for both environments. Nevertheless, when considering a 75.5% threshold of a single salt, the risk is higher in a rural environment, whereas this is the case for the urban environment when considering a 65.5% threshold for NaCl in a salt mixture (of course, such conclusions are overall depending on the general climate of the area).

## 4. Conclusions

The research presented supports improved understanding and prediction of salt weathering over time to underpin risk assessment. The importance of considering salt kinetics when estimating the number of crystallization cycles in a given environment is influenced by factors such as the exposed surface area of crystal(s)/solution (unconfined versus confined), the behavior of a single salt versus mixture, the resolution and location of climate measurements. Specifically, as concluded from the experimental data, dissolution processes take longer compared to crystallization, the former further enhanced considering an in-depth pore delay. Thus, considering dissolution above crystallization to determine the spatial (time) resolution in climatic data results in a more accurate approach.

The determination of relevant RH threshold(s) ( $RH_{eq}$  for a single salts or equilibria for a salt mixture) is also a critical factor. For NaCl the calculations show how the  $RH_{eq}$  drops when found in a common salt mixture and affects the accuracy of the prediction and reliability of the model. It has also been shown that specific location data is crucial for the assessment and that climate data at low spatial resolution can significantly influence the frequency of cycles. Seasonal buffering demonstrates the importance of the urban context and microclimates, rather than typically using measured meteorological data.

These results illustrate how the use of an indicator based on a single salt does not represent the more common real-world scenario of salts present in a mixture. The application of a simple indicator (threshold, based on a variable 'averaging window' of time) demonstrates a significant difference in estimated number of cycles. The findings are fundamental to improve appropriate timescale windows and illustrate a methodology with specific points of interest to quantify salt crystallization cycles in realistic environments as a risk assessment procedure that can be applied to climate data. Of additional interest is the potential to build upon the proposed method by incorporating one or a combination of other important factors and assessment approaches, including salt mixtures, pore and salt filling properties, extended climatic factors, boundary conditions, urban heat island effects, climate projections, and hygrothermal simulation.

## Declarations

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## Figures

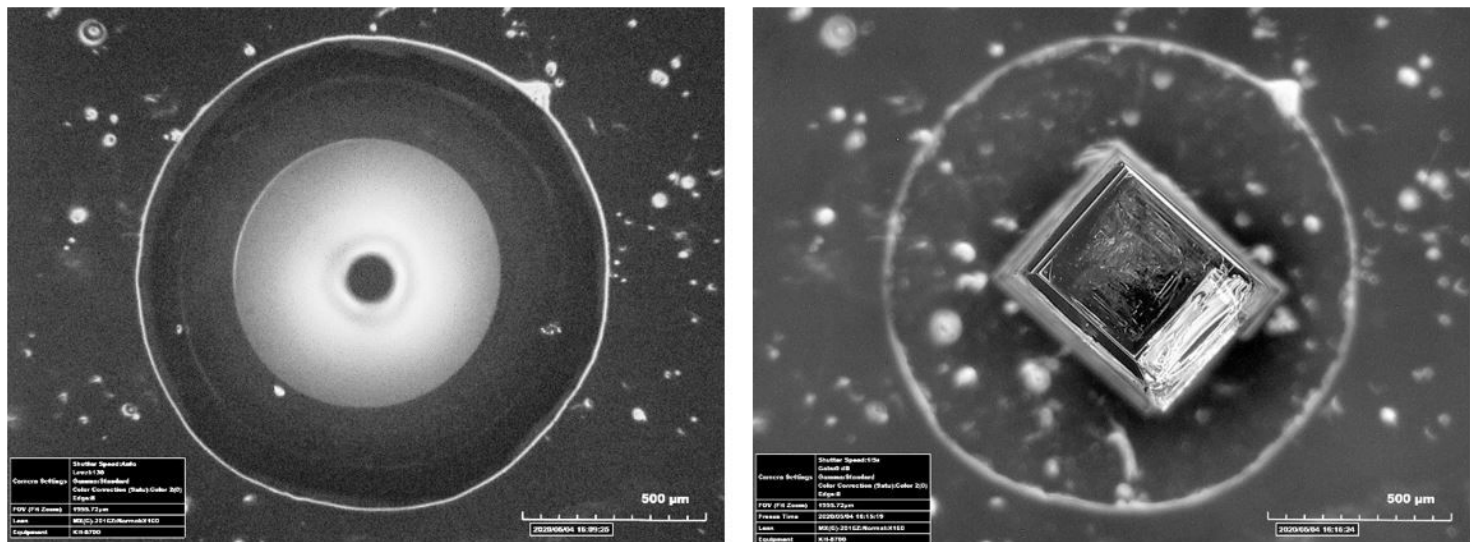


Figure 1

Example images of the droplet experiment (left) NaCl solution at 90% (start RH) and (right) completed crystallization of NaCl at 70% (target RH) visualized with digital microscopy (HIROX) in a microclimate chamber (GenRH/Mcell).

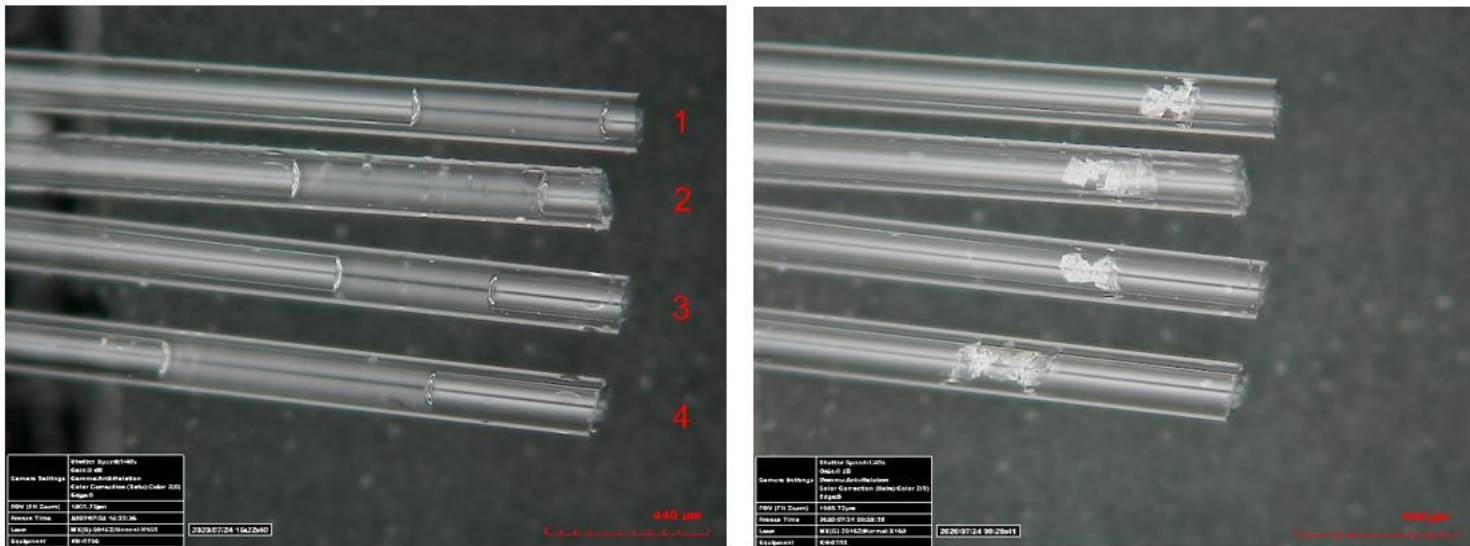
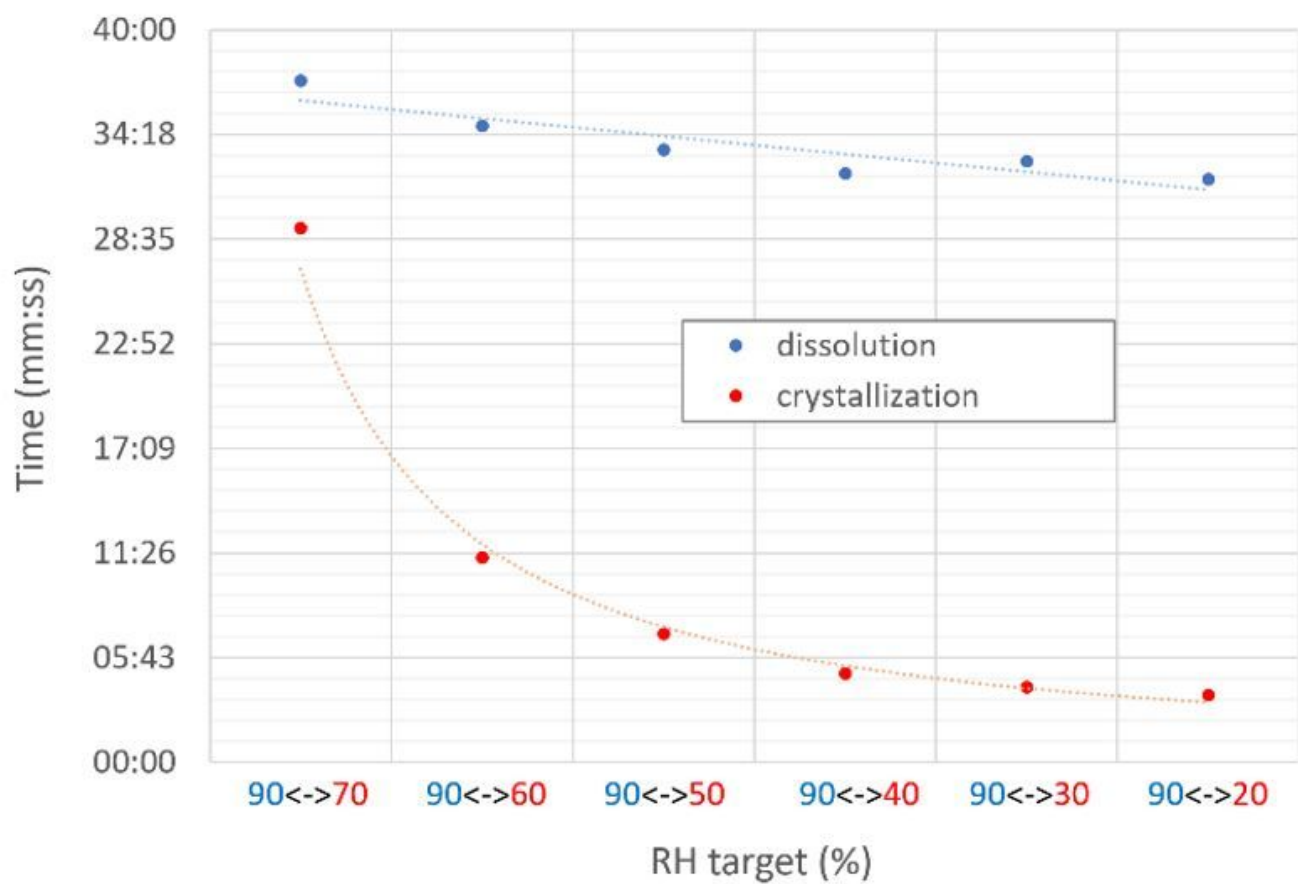


Figure 2

Example images of capillary experiments (left) NaCl solution at 90% (start RH) and (right) completed crystallization of NaCl at 20% (target RH), visualized with digital microscopy (HIROX) in a microclimate chamber (GenRH/Mcell).



**Figure 3**

Crystallization and dissolution times of unconfined NaCl crystal/droplet, determined by (GenRH/MCell; Hirox) at different RH targets between (90 and 20 %).

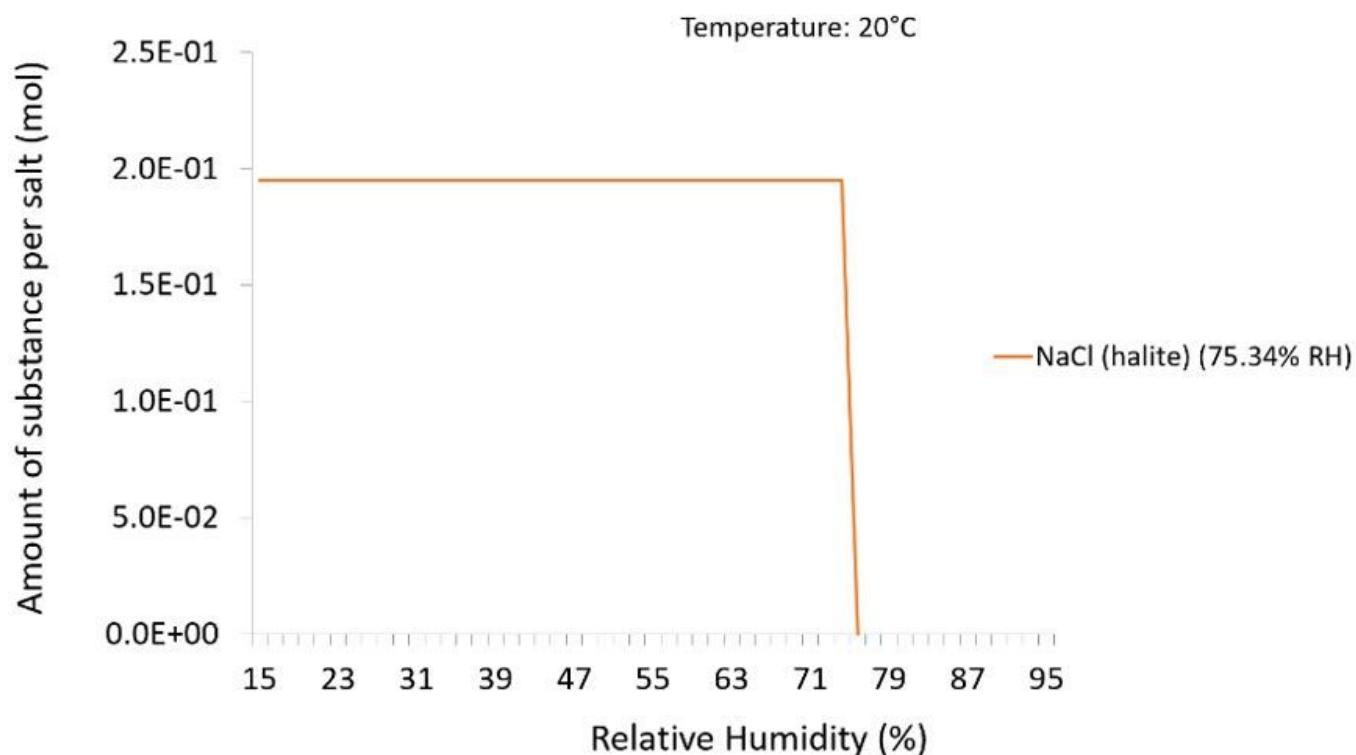


Figure 4

Behavior of NaCl between 15 and 95% RH at 20 °C (amount of substance represented as mol), modified ECOS/RUNSALT output. The legend shows sodium chloride with its respective RHeq.

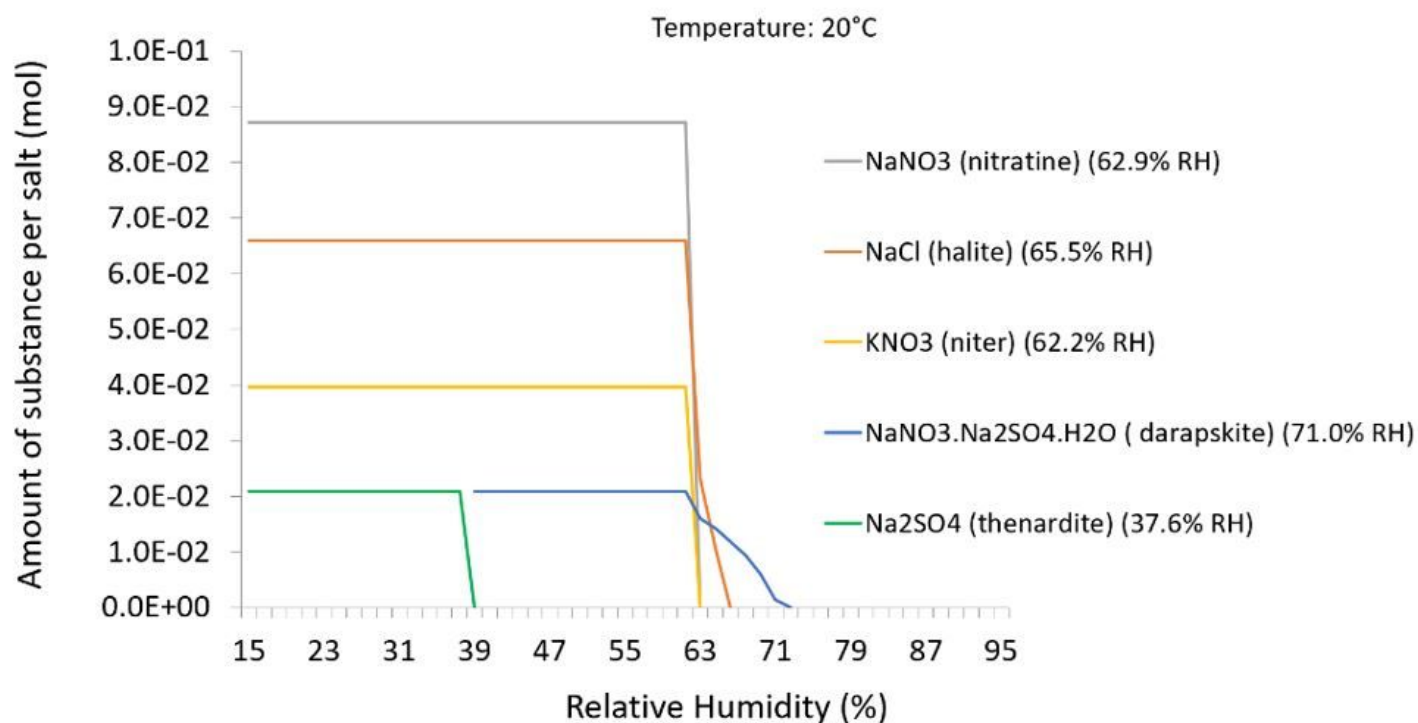


Figure 5

Behavior of NaCl in a common salt mixture under changing climate conditions, between 15 and 95% RH at 20 °C (amount of substance as mol/per salt), modified ECOS/RUNSALT output. The legend shows the specific salts with their respective RHeq.

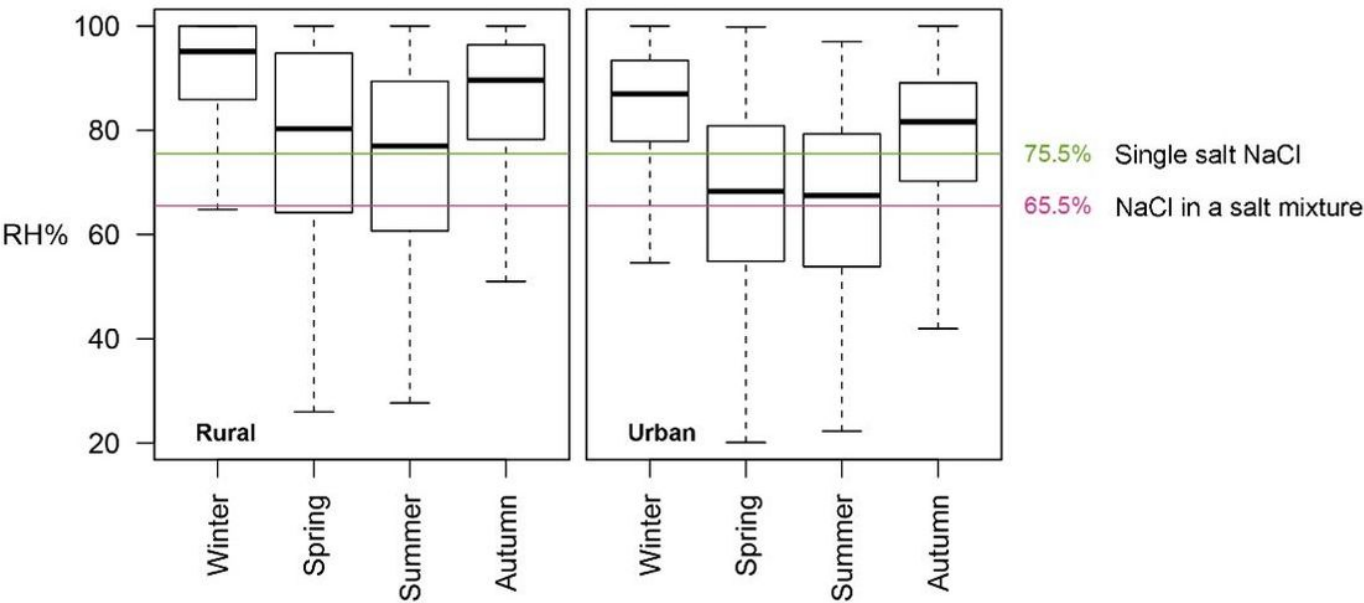
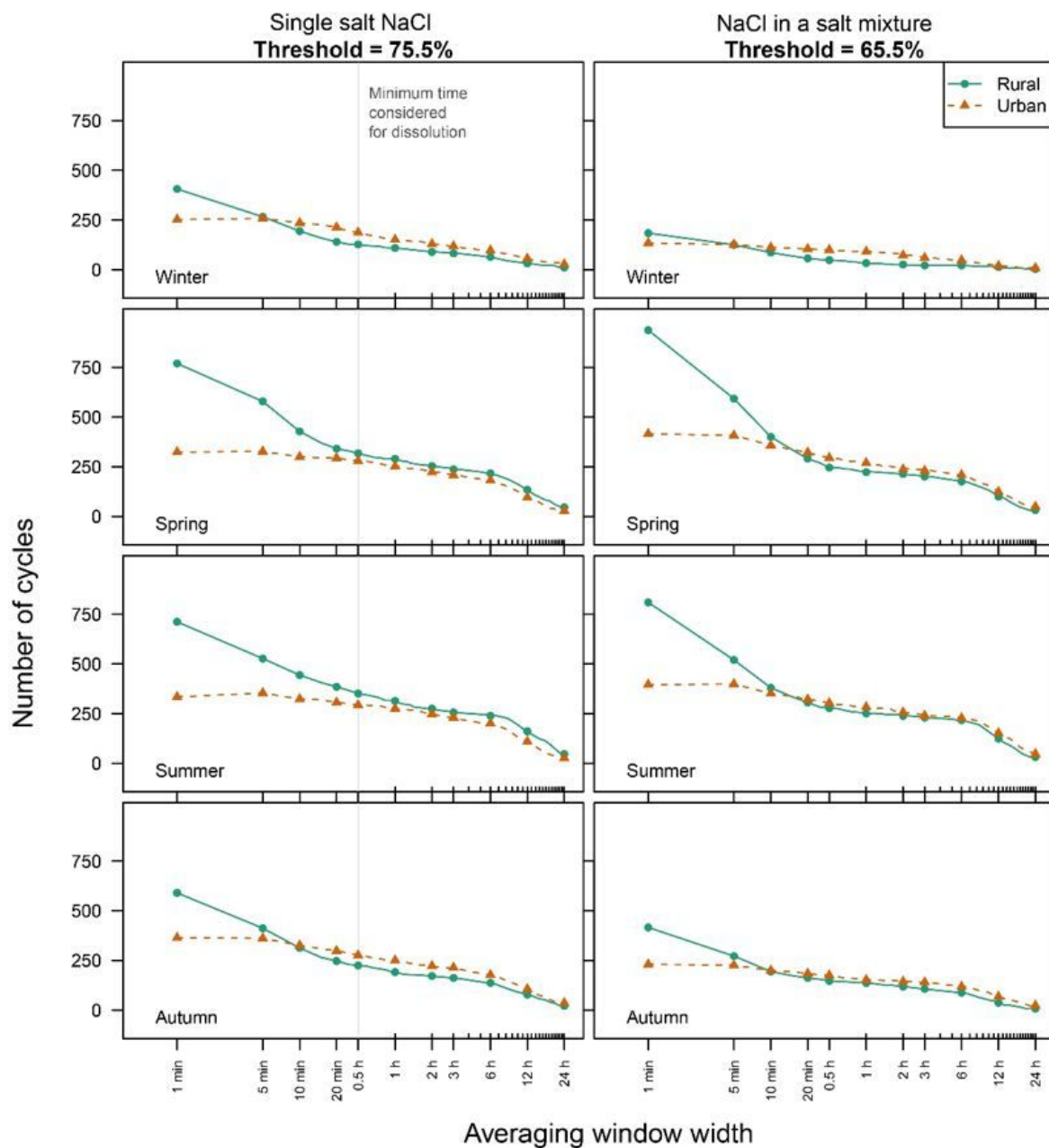


Figure 6

The RH distributions and average (black lines in the box plots) per season in rural (Melle, Belgium, 2016) or urban (central Ghent, Belgium, 2016) environments, demonstrating that the rural/urban difference of expected crystallization is most pronounced in spring and summer since the threshold of 75.5% and 65.5% is crossed.





**Figure 7**

Number of dissolution/crystallization cycles of NaCl per season in a rural (Melle, Belgium, 2016) or urban (central Ghent, Belgium, 2016) environment considering an average time scale between 1 min and 24 h when the RH threshold of 75.5% (representing pure NaCl) or 65.5% (representing NaCl in a mixture) is surpassed (x-axis in log scale).